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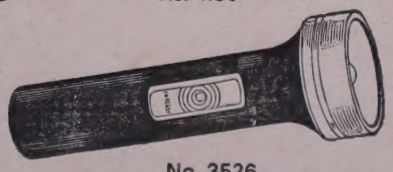

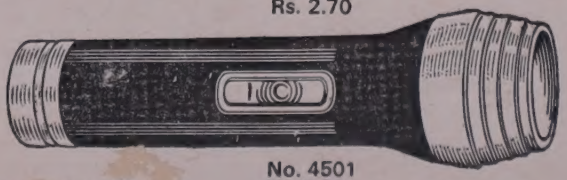

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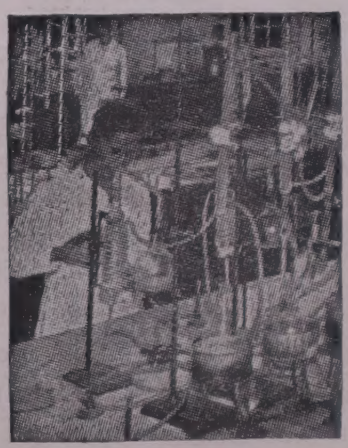

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NOTICE

EXAMINATION FOR THE ASSOCIATESHIP

Group A (Analytical Chemistry)

1. A.I.C. by examination is recognised as equivalent to M.Sc. degree in chemistry for purposes of recruitment of chemists as per G.O. No. F. 18—36/57-T-5, dated 19-8-58 of the Ministry of Scientific Research and Cultural Affairs. The examination with Section 2 (Drugs and Pharmaceuticals) is duly recognised in the Drugs Rules, Government of India. The eighteenth Examination is expected to be held at Calcutta in or around November, 1968, and will comprise of Theoretical, Practical and Oral tests.
2. In addition to General Chemistry (compulsory), Group A is divided into the following Sub-groups and Sections. Candidates will be required to select two subjects from amongst these (not more than one from a single Sub-Group) :

Sub-Group	*Section*	*Subject*
I	1.	Analysis of Minerals, Silicates, Ores and Alloys.
	3.	Analysis of Foods.
	9.	Analysis connected with Forensic Chemistry.
	10.	Analysis connected with Leather Chemistry.
II	2.	Analysis of Drugs and Pharmaceuticals.
	4.	Analysis of Water and Sewage.
	11.	Analysis connected with Textile Chemistry.
III	5.	Biochemical Analysis.
	6.	Analysis of Oils, Fats and Soaps.
	7.	Fuel and Gas Analysis.
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3. Number of theoretical papers is four, each of three hours' duration (Full Marks—100 in each ; Pass Marks—40% of total of theoretical). Paper I contains questions in two parts, one on organic and the other on inorganic chemistry. Paper II also contains questions in two parts, one on physical and the other on general analytical chemistry. Papers III and IV are on the two sections of applied analytical chemistry chosen by a candidate.
4. Each candidate is required to appear at practical examinations in the two sections chosen by him. The practical examination in each section continues for two days—six hours a day (Full Marks—300 in each ; Pass Marks—50% of total of practical).

5. The candidate for the 1968 examination will be required to register his name not later than 30th November, 1967, by submitting application in appropriate form and payment of a registration fee of Rs. 15/-. The candidate will also be required to submit the following with his application :—

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6. The examination fee is Rs. 75/-. The last date for submitting the fees is 31st May, 1968. Question papers of previous years are available at Rs. 2/- per year and the Syllabus at Re. 1/- per copy.

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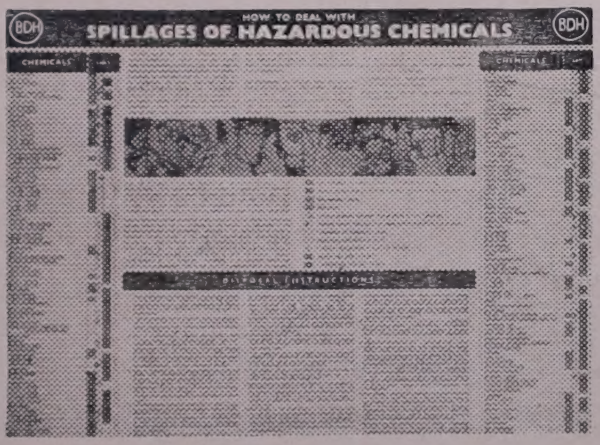

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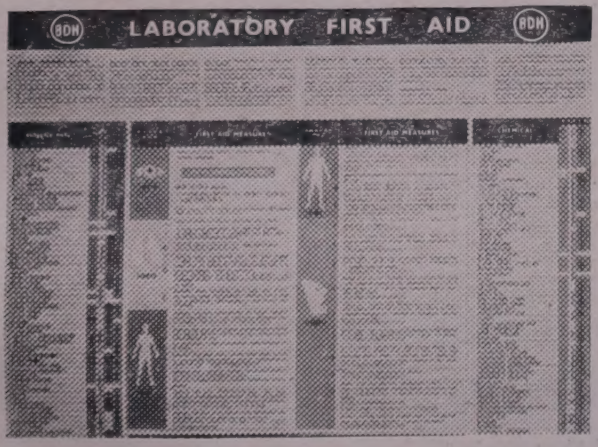

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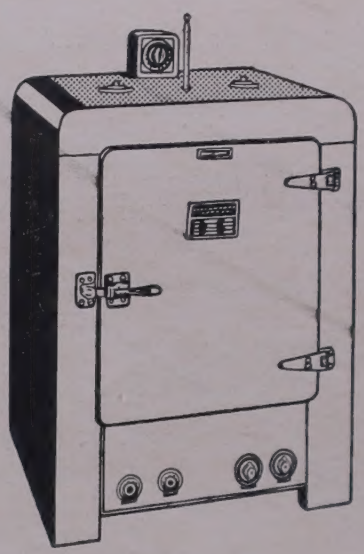

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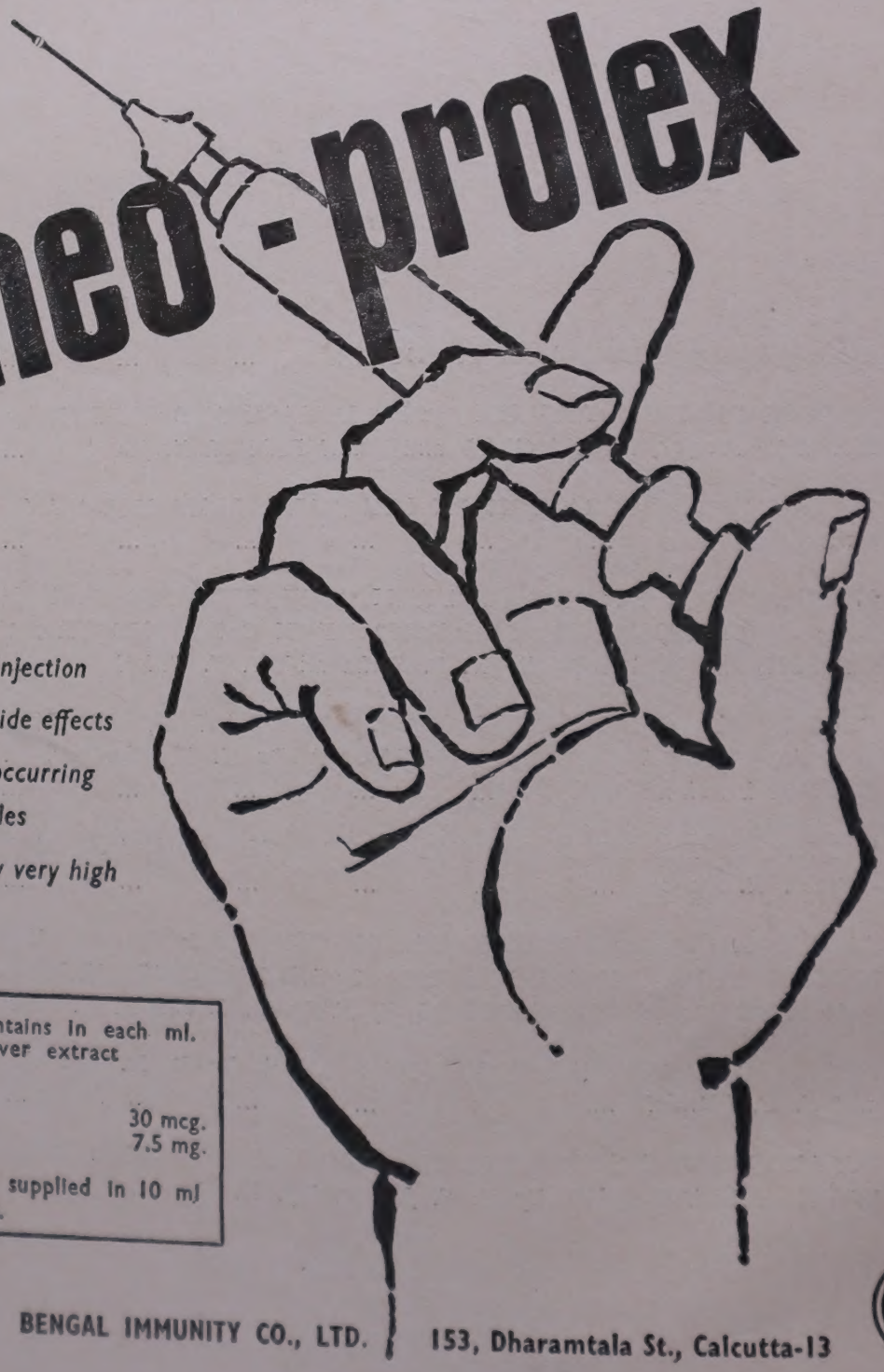

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FOODS FROM PETROLEUM PRODUCTS

An article on the subject in the Statesman dated 29 April 1967 makes very interesting reading in the light of the present World shortage of food. It has been reported that under favourable conditions high-protein yeasts can be successfully grown in some petroleum products like petrolem waxes and paraffins. Pilot plants are already in existence in several countries for further research and to work out economic feasibility. Useful products like the amino acids, vitamins, nucleic acids, etc. may also be obtained from the biological mass produced on petroleum. Extensive feeding trials are said to be carried out using test animals over several generations to ascertain the edibility of such products. However, it must be realised that such experiments are time-consuming and quick results may not be forthcoming. Particularly, one has to remember that for edibility the new products may have to satisfy stringent standards of World Bodies like the FAO/WHO. But, it is expected that they will ultimately augment to a great extent World supply of protein foods. Admittedly, intense work is needed on the many aspects of the problem which will require the services of chemists, technologists, biologists and scientists of other branches of science.

The connection of petroleum with food may not be an altogether new idea. Already, we see the successful use of petroleum hydrocarbons in the edible oil industry. These hydrocarbons of special purity are being widely and economically used for extraction of edible oils giving us increased supply of edible oil cakes. Let us hope that in the very near future foods from petroleum will be a routine thing.

S. N. M.

J. Inst. Chemists (India), Vol. XXXIX, September, 1967

A NOTE ON THE STABILITIES OF AMYLASE AND PEPSIN

By

RABINDRA MOHAN CHATTERJEE, NAVAJIT GHOSE AND KANTI PADA CHATTERJEE

Research Division, East India Pharmaceutical Works Ltd. Calcutta 34

(Received for publication on 10-11-'66.)

It is very difficult to put amylase and pepsin together in vitro in an active state for a sufficiently long period. Their optimum pH are quite dissimilar. The present communication deals with an investigation on the stability of fungal amylase with and without pepsin. Wheat bran was inoculated with a strain of Aspergillus Oryzae. After necessary incubation at 29°C, the bran was extracted with alcohol (10%) and with a mixture of alcohol (10%) and glycerol (25%) separately. Different periods of extraction were 4 and 20 hours. Enzymes produced from these extracts were fungal amylases, i.e. mixtures of alpha- and beta-amylase. One portion of the extracts from 4 hours' was treated with 0·1 calcium chloride. Amylase activities of these samples, stored at room temperature, were determined periodically. The present study was concerned with the dextrinogenic activity of the enzymes and the achromic point of the different enzyme concentrations were determined according to Hawk *et al*[1]. Results are given in Table 1. Concentrations of fungal amylases in different extracts did not vary much from each other. They were 18 ± 2 units of amylase per ml. pH was adjusted to 6·8 (approx.).

A number of mixtures of pepsin (4%) and amylase extract (18 ± 2 units of amylase/ml) were prepared. The solvent was a mixture of alcohol (10%) and glycerol (25%). These mixtures were supplemented with either citrate buffer (a), or antiseptic e.g. merthiolate—0·01% (b) or salt e.g. disodium phosphate —1% (c). pH of these mixtures was adjusted to 5·2 approximately. After 28 weeks at room temperature, some portions of (c) were taken out and stored at 10°C. Activities of pepsin[2] and amylase were determined periodically. Results are given in Table—2. 4% pepsin (Orthana Kemisk Saprik, Copenhagen, Denmark) in the mixture of alcohol (10%) and glycerol (25%), pH 5·2, was also stored at room temperature. Periodic determination showed no deterioration in the activity for 100 weeks.

From the results it would be noted that the extracts from the mixture of solvents were found to possess more stable form of amylase activity than those obtained by extraction with alcohol only (Table-1). 4 hours' extraction was as satisfactory as that of 20 hours'. Addition of trace amount of calcium chloride in the extract did not improve upon the stability. Fukumoto[3] reported that calcium salts were very effective in protecting amylase from inactivation

TABLE 1

Amylase activities of different extracts, stored at room temperature (Initial activities of different extracts were 18±2 units of amylase/ml.)

Period (weeks)	Alcohol (10%) extract		Alcohol (10%) and Glycerol (25%) extract		
	4 hrs.	20 hrs.	4 hrs.	20 hrs.	4 hrs. with $CaCl_2$
	%	%	%	%	%
4	8	10	90	89	90
8	0	0	85	83	84
16	0	0	82	80	84
24	0	0	75	70	80
32	0	0	75	68	75
40	0	0	70	68	75
50	0	0	65	66	70
75	0	0	62	60	65
100	0	0	58	55	60

Percentages of activities were calculated on the basis of initial values.

TABLE 2

Pepsin and amylase activities of different samples stored at room temperature (A=amylase activity, B=Pepsin activity)

Period (weeks)	No (a)		No (b)		No (c)	
	A	B	A	B	A	B
	%	%	%	%	%	%
4	29	100	36	100	100	100
8	12	100	12	80	90	100
12	5	100	5	80	90	100
16	3	80	3	80	80	80
20	2	80	2	80	80	80
28	0	50	0	50	80	50
36	0	40	0	50	70	50
50	0	40	0	50	70	50
75	0	34	0	34	50	20
100	0	28	0	28	40	15

pH of the samples did not change significantly during the period of investigation. Percentages of activities were calculated on the basis of initial values.

during its storage in a concentrated solution. The present investigation was not concerned with a pure form of enzyme but with an admixture of certain other materials which might have prevented calcium salts in effecting its protective influence. Certain amount of disodium phosphate in effecting its protective influence. Certain amount of disodium phosphate was found very effective in controlling the rapid deterioration of the activities of the two enzumes (Table 2). At 10°C, very little change in the activities were observed for another 100 weeks.

The authors are grateful to Mr. P. Bagchi, Research Director, East India Pharmaceutical Works Ltd., Calcutta, for his helpful suggestions and encouragement.

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J. Inst. Chemists (India), Vol. XXXIX, September, 1967

EFFECT OF TEMPERATURE ON MINERAL FILLED NOVOLAK

By

D. P. Basu

Plastic Powders Private Ltd, Calcutta

(Received for publication on 6-12-66.)

Summary

Effect of heating at different temperatures and for different periods on the curing time of mineral filled Novolak (acid catalysed phenol Formaldehyde resin) was studied. Curing time can be reduced by heating the material at a suitable temperature and the effect of heating is similar for compositions using different minerals.

Curing time of a resin is of great industrial importance. When the resins are used for production of articles (mouldings or laminates) the process of reducing curing time becomes an important factor. More finished items can be produced within the same time cycle using a resin of less curing time. In the case of preparing moulding powders from resin the compound containing resin, filler, hardener, etc., is rolled on the roll mill heated by steam to get the resin coated on the filler as well as to reduce the curing time. In the case of laminating resins the reduction in curring time is attained by heating the resin to a greater consistency or viscosity. As a result of heating a thermosetting resin in the presence of hardner chain lengthening as well as crosslinkage starts and the extent of such reactions governs the curing time of the material at that time. Houwink,[1] Megson,[2] Barkhuff and Carswell[3] and others have studied the mechanism of polymerisation and phenoplast structure in detail. On heating the mineral filled resin also the curing time of the material is reduced as it happens in the case of moulding powders or laminating resins. Mineral fillers are used as fillers for imparting high heat resistance, chemical resistance, exceptional electrical properties etc to the Novolak. The use of minerals in phenoplast has been studied in detail by Cummins'[4] McMurray[5] and others.

Preparation of Novolak[6]

Phenol and formaldehyde (37% by weight) in a molecular ratio (1 : 0·8) were mixed with oxalic acid 1·5% on the weight of phenol and charged into the reaction kettle which was fitted with steam jacket, reflux condenser and stirrer. Temperature in the kettle was allowed to rise for 15-20 minutes to 65-70°C by passing steam gently. Refluxing was continued for 60 minutes

and then the distillation was started. Distillation was continued until a "sample" cooled was found non-tacky and brittle. The resin was run out of the kettle into trays to cool. The resin thus obtained was pale yellow in colour, had softening range 60-70°C and soluble in alcohols, esters and ketones.

Preparation of Mineral Filled Novolak

Amongst mineral fillers, mica and asbestos are widely used in making Phenolic moulding powders and properties of powders using these fillers have been widely studied. In our experiments, minerals which are not commonly used in making moulding powders were used ; cheap minerals like slate and kieselguhr were used to make the resin compositions. The two minerals are widely different in nature. Kieselguhr is hydrated silica and very light in weight whereas slate is natural form of aluminium silicate having appreciable density.

Powdered Novolak was mixed with Hexamine and lime in the ratio of 16 : 2 : 1 parts by weight. The resin base thus produced was next compounded with different minerals to produce different compositions for heat treatmet.

Composition I—Resin base 19 parts and Kieselguhr 20 parts. .....(A)

Composition II—Resin base 19 parts and slate powder 20 parts .....(B)

The compound thus produced was next heated in a tray in a thermostatically controlled air oven at different temperatures.

e.g. $70 \pm 1°C$, $90°C \pm 1°C$, $110° \pm 1°C$, $130°C \pm 1°C$

Amount of material taken for each experiment was 100 gms. It was spread over the tray into a layer of 1cm thickness. At each temperature while the material was heated, a sample was withdrawn from the tray at intervals of 1 hour and curing time of the compound was determined. To determine the curing time, 1 gm of the sample was made into a paste with 0·2 ml methylated spirit and heated till the material hardened. Time required by the material to harden at the boiling temperature of the mass was taken as the curing time of the material.

Results and Discussions

Results of the above experiments are shown in Fig. I and Fig. II.

In *Fig. 1*, the curing time was plotted against hours heated. Two curves were plotted for compositions I & II. It is evident from these curves that at first there is a sharp fall in curing time and then the curing time falls slowly or remains almost constant until it is cured. It was also observed that the fall in curing time is greater and more rapid the higher the temperature. Thus, at 110°C ± 1°C material was found to remain uncured even after heating for 18 hours. At and above 130°C the change in curing time is very rapid; at 160°C the material was cured within minutes.

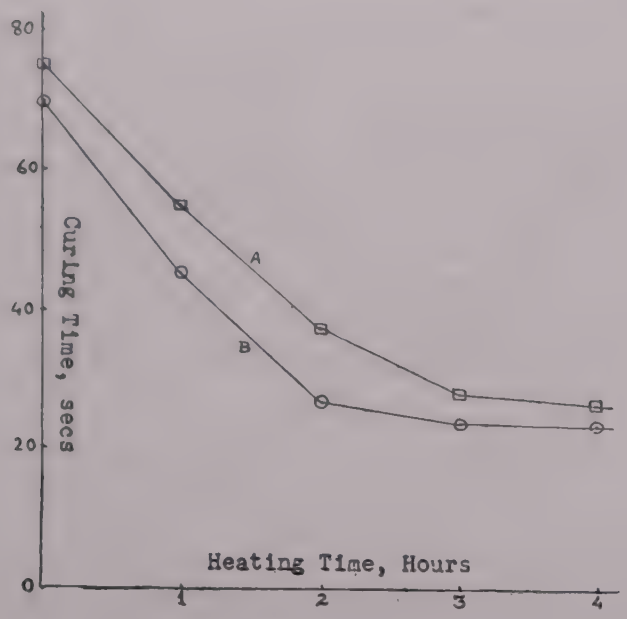

FIG. 1
Results of heating at 130°C.
A. Composition using kieselguhr.
B. Composition using slate.

From these results it is evident that heating at 130°C for 1-2 hours is more convenient and industrially feasible to reduce the curing time.

In *Fig. 2,* curing time of the mixture after heating for 1 hour at different temperature was plotted against temperature. Heating for 1 hour at 70°C has no effect on curing time. On heating above 70°C the curing time starts to fall. The rate of fall becomes appreciable above 90°C and remains so upto 135°C.

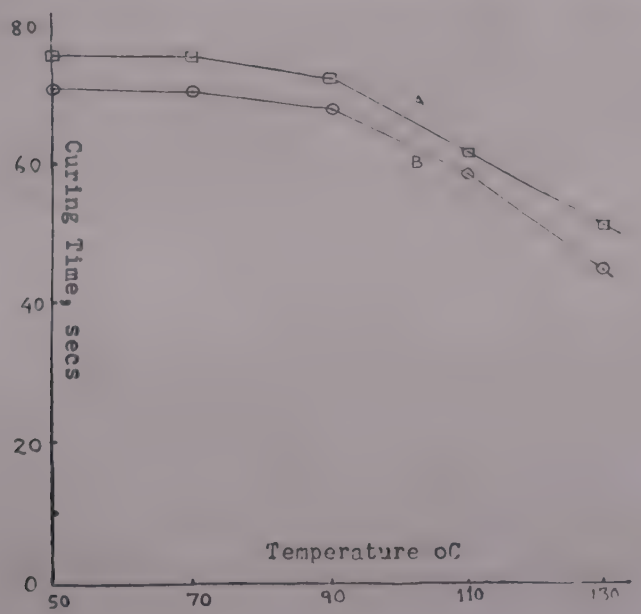

FIG. 2
Effect of heating for one hour at different temperature.
A. Composition using kieselguhr.
B. Composition using slate.

But all the compositions were found to be cured on heating for 1 hour at 140°C. Although slate and kieselgurh have widely different properties the result of heating in both the cases is similar as is evident from Figs. I & II. Kieselguhr which is a mass of hydrated silica has got similar behaviour towards Novolak as slate which is natural form of aluminium silicate. Even the porous nature of kieselguhr does not seem to affect the nature of the curve. As there is no evidence of chemical reaction between the resin and mineral fillers the change in curing time with temperature is dependent on the chemical changes taking place on heating the resin.

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NITRIFICATION STUDIES ON NEEM CAKE, MIXTURE OF NEEM CAKE AND SUPERPHOSPHATE, PROCESSED NEEM CAKE AND THEIR EFFECT ON SOIL AGGREGATION

By

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Oil seeds constitute economic crop in India and oil cakes constitute valuable by-products of the oil extraction industry, which is utilised both as cattle feed and manures. The edible cakes are more profitably utilised as cattle feed and non-edible ones are used as manure.

Oil cakes are rich sources of nitrogen, phosphate and potash, and also contain other essential elements. Besides, they also add a small amount of organic matter to the soil which improves the physical condition of the soil. Organic matter added to soil, besides other properties, helps to improve the soil structure by affecting soil aggregation in course of their decomposition They have low C/N ratio and hence, their mineralisation takes place at a rapid rate thereby releasing nitrogen for the growing plant (Lyon and Buckman).[1]

Among the non-edible oil cakes, neem, castor, mahua, karanj, are important. India possesses a large number of perennial trees of neem, mahua and Karanj. Of these neem trees are outstanding owing to their availability in abundance, can grow even on poor soils and above all their medicinal properties.

Neem seed cake which is left after expression of oil is extensively used as manure. The use of this cake will simultaneously help towards easing the cost factor of the main product. Neem seed cake contains some residual bitters and foul-smelling odoriferous constituents and so is unfit for cattle feed. The entire quantity of the neem seed cake produced by villagers is consumed as manure. The cake is sometimes preferred for manuring certain crops, such as, sugarcane for its supposed manurial and insecticidal properties. No work for processing the cake has been carried out apart from its analysis for nitrogen, phosphate and potash for its evaluation as manure.

A certain amount of oil depending on the process of extraction is invariably left in the oil cake but this does not affect their manurial value. Work on this

aspect reported by Puranchandra and Shrikhande[2] showed that oil content upto 7% in castor and neem cakes had no adverse effect on the process of nitrification.

Pal and Rakshit[3] observed that addition of lime quickens nitrification. Vaidyanathan[4] while summarising the results of manurial trials in India pointed out that oil cakes and superphosphate gave better yield than oil cakes alone.

Material and Methods :—The neem seed cake used in the present investigation was obtained from Ballabgarh, Adarsh Cooperative Gramudoyog Centre, Tigaon Road, Ballabgarh and Principal, Harcourt Butler Technological Institute, Kanpur through the good officers of Indian Central Oil Seeds Committee.

The cake used for nitrification tests were well powdered and made to pass through 1mm sieve. Air-dry soil samples were ground in a porcelain mortar with a wooden pestle and sieved through 2-mm sieve.

The cakes were extracted with alcohol by soxlet extraction method. Cakes were added to the soil @ 30 mgm per 100 gm of soil. The empty bottles were weighed and filled up with the mixture of soil and cakes and again weighed finally. Moisture was maintained at ⅓rd. saturation capacity of the soil and this was made up every week, by making up the loss in the weight of the bottles by adding water. Ammoniecal -N, No_2-N and No_3-N were estimated after an interval of 15 days. There were two replications and average of the two were taken (Wright)[5]. Aggregate analysis was done by Martin and Waksman method[6].

Experimental findings :—Ammonia production in soil treated with neem cake, neem cake cum superphosphate and processed neem cake are given below :—

TABLE 1

Treatments	NH_3 in mgm per 100 gm of soil					
	Days					
	15	30	45	60	75	90
Control	2·9	3·4	4·3	4·2	4·0	2·5
Neem cake	8·7	10·5	11·2	9·8	6·8	5·6
Neem cake *cum* S.S.P.	9·8	11·2	13·4	10·2	7·6	4·7
Processed neem cake	10·9	12·7	11·3	9·4	6·9	5·0

Nitrite produced at different intervals in treated soil are detailed in Table 2.

TABLE 2

Treatments	No_2 — N in mgm per 100 gm of soil					
	Days					
	15	30	45	60	75	90
Control	Trace					
Neem cake	2·1	1·8	0·5	Tr.	Tr.	Tr.
Neem cake *cum* S.S.P ...	2·0	1·9	0·3	—	—	—
Processed neem cake ...	1·8	0·8	0·2	—	—	—

Nitrate produced at different intervals is given in Table 3.

TABLE 3

Treatments	No_3—N in mgm per 100 gm of soil					
	Days					
	15	30	45	60	75	90
Control	2·5	3·0	4·1	4·2	4·2	4·3
Neem cake	6·2	9·3	10·5	13·0	13·5	14·2
Neem cake *cum* S.S.P.	7·3	10·8	11·2	13·2	15·6	15·4
Processed neem cake	8·2	11·3	13·5	16·7	16·6	16·5

Water stable aggregate :—The effects of neem cake with respect to processed cake and neem cake with superphosphate on development of soil structure were also studied at interval of 30,60 and 90 days. Results obtained are given in table 4 in percentage of water stable aggregates.

TABLE 4

Treatments	% water stable aggregates Days		
	30	60	90
Control	67·2	68·4	68·6
Neem cake	86·2	82·4	79·7
Neem cake with S.S.P. ...	82·1	78·3	73·5
Processed neem cake ...	80·0	76·4	72·2

The percentage of water stable aggregate throughout the period of observation (90 days) is practically the same in control soil, whereas, in treated soils water stabled aggregates are maximum 30 days and gradually decreasing afterwards.

Discussion :—Nitrification studies were carried out on neem cake, neem cake with superphosphate and processed neem seed cake in Delhi soil in order to find their superiority for manurial use. A study of the comparative rate of nitrification of the cakes reveals that after 60 days maximum nitrification was observed in processed neem seed cake, followed by neem cake with single superphosphate and neem cake as such. The low nitrification of neem cake may be due to higher fat content and presence of high percentage of non-fatty matter (bitters and odoriferous substances) in the cake. This is in conformity with the findings of Shrik hande[7]. Early nitrification of the extracted cake can also be explained due to removal of these components.

The nitrification of neem cake has been observed to increase in combination with single superphosphate by 7% over neem cake alone. Thus, it is found that single superphospate had a favourable effect on nitrification. Vaidyananthan (1934) had also reported that neem cake in combination with single superphosphate gives higher yield than neem seed cake alone.

The experimental data in Table 4 reveal that the effect of oil cakes on water stable aggregate does not seem to last long. This is in conformity with the findings of previous workers who have observed that quick decomposing organic manures did not have lasting effect on water stable aggregates (Browing and Milam)[8]. The highest percentage of water stable aggregate (86·2%) is in neem cake treated soil followed by neem cake with single superphosphate (82·1%) and processed neem cake (80·0%) at the end of 30 days and then there was gradual decline. This suggests that chemical fertilizers have depressing effect on formation of water stable aggregates.

Summary :—By suitably processing neem seed cake, its manurial value may be increased. The addition of phosphate with cake also enhances its nitrifying capacity. The effect of cakes on formation of water-stable aggregates is temporary. However, this aspect requires further investigation with a view to work out the economics of the whole process.

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STUDIES IN ISOFLAVONES-PART I. BROMINATION, IODINATION AND NITRATION OF 7-HYDROXYISOFLAVONE

By

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Various substitution reactions on benzo-α-and γ- pyrone derivatives are being studied in this laboratory with a view to see the pattern of substitution and to prepare intermediates for further synthetical work. Neither the halogenation nor the nitration of isoflavones, appears to have been systematically studied so far. The present work deals with the bromination, iodination and nitration of 7-hydroxyisoflavone.

7-Hydroxyisoflavone (I) with one molecule of bromine gave the 8-bromo derivative which on methylation and subsequent hydrolysis gave 2-hydroxy-4-methoxy-3-bromo phenyl benzyl ketone, the methyl ether of which was identical with the product obtained by the condensation of 2-bromo resorcinol with phenylacetylchloride and methylation of the bromo ketone formed. With four molecules of bromine, (I) gave the 6, 8-dibromo derivative which on methylation and hydrolysis gave 2-hydroxy-4- methoxy-3, 5-dibromo phenyl benzyl ketone, the methyl ether of which was identical with the product obtained on methylation of the ketone obtained from 2, 4-dibromo resorcinol and phenyl acetyl chloride. With liquid bromine, (I) furnished a tribromo derivative. Its methyl ether on hydrolysis gave 2-hydroxy-4-methoxy-3, 5-dibromo phenyl benzyl ketone and benzoic acid indicating that the third bromine atom was in neither of the benzene rings. 7-Hydroxy-2, 6, 8-tribromo isoflavone structure has therefore been assigned to this product.

(I), on iodination with one molecule of iodine and iodic acid or with iodine and ammonia, afforded the 8-iodo derivative. Its structure was established by methylation and subsequent hydrolysis to 2-hydroxy-4-methoxy -3-iodo-phenyl benzyl ketone, identical with the product obtained on condensation of the dimethyl ether of 2-iodo resorcinol[1] with phenyl acetyl chloride. Partial demethylation took place in the course of the condensation. With excess of iodine and iodic acid (I) gave a diiodo derivative to which the 7-hydroxy-6, 8-diiodo isoflavone structure has been assigned as its methyl ether on oxidation with alkaline potassium permanganate gave benzoic acid and on hydrolysis gave a diiodo derivative which was identical with the product obtained on iodination of 2-hydroxy-3-iodo-4-methoxy phenyl benzyl ketone with iodine and iodic acid.

On nitration with fuming nitric acid in acetic acid at room temperature, (I) gave the 8-nitro derivative, identical with the product obtained by the condensation of ethyl orthoformate with 2, 4-dihydroxy-3-nitro phenyl benzyl ketone, which in turn was obtained from the Fries rearrangement of the diphenyl acetoxy derivative of 2-nitro resorcinol. 7-Methoxy-isoflavone under the same condition did not undergo nitration.

(I) and its methyl ether, on nitration with a mixture of nitric acid and sulphuric acid at 0-5° gave the known 4'-nitro derivatives, previously synthesised by Karmarkar[2] from 2, 4-dihydroxyphenyl-4'-nitro benzyl ketone[3]. On nitration with the same reagents at 5-10°, 7-methoxyisoflavone gave the 8, 4'-dinitro derivative, identical with the product obtained on nitration of 7-methoxy -8-nitro-and 7-methoxy-4'-nitro isoflavone with nitric acid-sulphuric acid mixture at 5-10°. 7-Hydroxy isoflavone on a similar nitration gave a dinitro derivative the methyl ether of which was identical with 7-methoxy-8, 4'-dinitro isoflavone.

Experimental

7-Hydroxy-8-bromoisoflavone : To a boiling solution of 7-hydroxyisoflavone (1·2 g.) in glacial acetic acid (10 ml.) was added bromine solution in acetic acid (10% ; 8ml.) and the reaction mixture was kept at room temperature for 2 hr. The product which separated was crystallised from acetic acid in white shining needles (1 g.), m.p. 253°. (Found : Br, 25·06, $C_{15}H_9O_3Br$ requires Br, 25·23%).

The methyl ether : Prepared by refluxing the above isoflavone with dimethyl sulphate and anhydrous potassium carbonate in acetone for 4 hr. was crystallised from acetic acid, m.p. 178°. (Found : C, 58·11 ; H, 3·50 ; Br, 24·58. $C_{16}H_{11}O_3Br$ requires C, 58·00 ; H, 3·32 ; Br, 24·17%).

2-Hydroxy-3-bromo-4-methoxyphenylbenzyl ketone : The above methyl ether (2 g.) was refluxed in ethanol with sodium hydroxide (10% ; 25 ml.) for 4 hr. and the product obtained on acidification was crystallised from acetic acid in white plates (1·6 g.), m.p. 198°.

(Found : C, 56·12 ; H, 4·44 ; Br, 25·37. $C_{15}H_{13}O_3Br$ requires C, 56·07 , H, 4·05 ; Br, 24·92%).

2, 4-Dimethoxy-3-bromophenyl benzyl ketone : Obtained by methylating the above product with dimethyl sulphate in acetone solution in the presence of anhydrous potassium carbonate as usual and crystallised from acetic acid gave m.p. 106°. (Found : C, 57·55 ; H, 4·42 ; Br, 23·79. $C_{16}H_{15}O_3Br$ requires C, 57·30 ; H, 4·47 ; Br, 23·80%).

2, 4-Dihydroxy-3-bromophenyl benzyl ketone : 2-Bromoresorcinol (2 g.) in nitrobenzene (20 ml.) was mixed with aluminium chloride (1 g.) in nitrobenzene at room temperature and phenyl acetyl chloride (1 g.) was gradually added to the reaction mixture which was then left overnight. Next day it was heated on a steam bath for 4 hr. and the nitrobenzene was removed by steam distillation. The residue obtained was washed with sodium bicarbonate and the product was crystallised from alcohol in white shining needles (1 g.), m.p. 195°.

(Found : C, 54.66 ; H, 3·22 ; Br, 25.77. $C_{14}H_{11}O_3Br$ requires C, 54·72 ; H, 3·58 ; Br, 26·05%).

7-Hydroxy-6, 8-dibromoisoflavone : To a hot solution of 7-hydroxyisoflavone (1·2 g.) in glacial acetic acid (20 ml.), bromine in acetic acid (10% ; 32 ml.) was added and the reaction mixture left overnight. It was then diluted with water and the product obtained was crystallised from alcohol in colourless needles (0·8 g.), m.p. 212°. (Found : Br, 40·22. $C_{15}H_8O_3Br_2$ requires Br, 40·4%).

The methyl ether : Prepared by methylating the above product with dimethyl sulphate in acetone solution in the presence of anhydrous potassium carbonate and crystallised from acetic acid gave m.p. 139°. (Found : C, 53·53 ; H, 2·88 ; Br, 38·87. $C_{16}H_{10}O_3Br_2$ requires C, 53·04 ; H, 2·76 ; Br, 39·02%).

2-Hydroxy-4-methoxy-3, 5-dibromophenyl benzyl ketone : The above methyl ether (1·0 g.) was hydrolysed by refluxing with alcoholic sodium hydroxide (10% ; 25 ml.) for 4 hr. The product obtained on acidification was crystallised from acetic acid in white needles (0·9 g.), m.p. 120°. (Found : C, 45·22 ; H, 3·42 ; Br, 40·13. $C_{14}H_{10}O_3Br_2$ requires C, 45·00 ; H, 3·00 ; Br, 40·00%).

The dimethyl ether : Prepared as before by refluxing with dimethyl sulphate in acetone solution in presence of anhydrous potassium carbonate and crystallised from petroleum ether gave m.p. 88°. (Found : C, 46·10 ; H, 3·72 ; Br, 39·05. $C_{16}H_{14}O_3Br_2$ requires C, 46·30 ; H, 3·38 ; Br, 38·66%).

2, 4-Dihydroxy-3, 5-dibromophenyl benzyl ketone : 2, 4-Dibromo resorcinol (2·0 g.) was condensed with phenyl acetyl chloride (1 g.) in presence of anhydrous aluminium chloride (1 g.) in nitrobenzene as described earlier. The product obtained was crystallised from benzene in yellow needles (1·1 g.), m.p. 190°. (Found : C, 46·33 ; H, 2·43 ; Br, 40·98. $C_{11}H_{10}O_3Br_2$ requires C, 46·10 ; H, 2·60 ; Br, 41·40%).

On methylation with dimethyl sulphate as before it gave the dimethyl ether. M.p. and mixed m.p. with the product described above was 88°.

7-Hydroxy-2, 6, 8-tribromoisoflavone : A mixture of 7-hydroxyisoflavone (1·2 g.) in hot acetic acid (20 ml.) and liquid bromine (2 ml.) was heated on a steam bath for 3 hr. The product obtained was crystallised from acetic acid in white plates (1·5 g.), m.p. 278°. (Found : Br, 50·26. $C_{15}H_7O_3Br_3$ requires Br, 50·52%).

The methyl ether : The above product was methylated as usual and the methyl ether was crystallised from acetic acid, m.p. 218°. (Found : C, 39·60 ; H, 2·10 ; Br, 49·10. $C_{16}H_9O_3Br_3$ requires C, 39·20 ; H, 1·80 ; Br, 49·00%)

The methyl ether on hydrolysis gave 2-hydroxy-4-methoxy-3, 5-dibromophenyl benzyl ketone and benzoic acid. The mixed m.p. of the ketone with an authentic sample prepared as described above was not depressed.

7-Hydroxy-8-iodoisoflavone : To a hot solution of 7-hydroxyisoflavone (1·2 g.) in alcohol (20 ml.) iodine (0·5 g.) in alcohol (5 ml.) and iodic acid (0·3 g.) in water (2 ml.) were added and the reaction mixture then stirred for half an hour. The product which separated was crystallised from alcohol in white shining needles, (1·1 g.), m.p. 250°. (Found : I, 35·02. $C_{15}H_9O_3I$ requires I, 35·0%).

The same compound was also prepared by iodinating 7-hydroxyisoflavone (1·2 g.) with iodine (0·5 g.) in the presence of ammonia and potassium iodide. The mixture was stirred at room temperature for half an hour. It was poured into excess of ice cold sulphuric acid and the separated product was crystallised from alcohol, m.p. 250°.

The methyl ether : 7-Hydroxy-8-iodoisoflavone (1·3 g.) was refluxed with dimethyl sulphate (0·6 g.) and anhydrous potassium carbonate (0·6 g.) in acetone (100 ml.) for 4 hr. The product was crystallised from acetic acid, m.p. 169°. (Found : C, 50.72 ; H, 3·36 ; I, 33·45. $C_{15}H_{13}O_3I$ requires C, 50·80 ; H, 2·90 ; I, 33·60%).

2-Hydroxy-4-methoxy-3, 5-diiodophenyl benzyl ketone : The above methyl ether (1·9 g.) was refluxed with ethanolic sodium hydroxide (10%; 25 ml.) for 4 hr. and the ketone obtained was crystallised from acetic acid in white shining needles, (1·5 g.), m.p. 217°. (Found : C, 48·72 ; H, 3·91 ; I, 34·30. $C_{15}H_{13}O_3I$ requires C, 48·90 ; H, 3·50 ; I, 34·50%).

The same ketone was obtained when to a mixture of the dimethyl ether of 2-iodoresorcinol[1] (2 g.) in nitrobenzene, anhydrous aluminium chloride (4 g.) in nitrobenzene and phenyl acetyl chloride (1 g.) were added with stirring and the reaction mixture was kept overnight. It was then heated for 2 hr. and worked up as usual.

7-Hydroxy-6, 8-diiodoisoflavone : To 7-hydroxyisoflavone (1·2 g.) in boiling alcohol (30 ml.), iodine (4·0 g.) in alcohol and iodic acid (0·25 g.) in water were added and the reaction mixture left overnight. The product obtained after pouring the reaction mixture in water was crystallised from alcohol in colourless needles (0·8 g.), m.p. 208°. (Found : I, 51·59. $C_{15}H_8O_3I_2$ requires I, 51·70%).

The methyl ether : Prepared from the above isoflavone and crystallised from aetic acid gave m.p. 210°. (Found : C, 38·40 ; H, 2·30 ; I, 50·46. $C_{16}H_{10}O_3I_2$ requires C, 38·00 ; H, 2·00 ; I, 50·40%).

2-Hydroxy-4-methoxy-3, 5-diiodophenyl benzyl ketone : The above methyl ether was hydrolysed as usual and the product obtained after acidification was crystallised from acetic acid, m.p. 140°. Found : C, 36·22 ; H, 2·22 ; I, 51·90. $C_{14}H_{10}O_3I_2$ requires C, 36·40 ; H, 2·40 ; I, 51·40%).

The same compound was also obtained when 2-hydroxy-3-iodo-4-methoxy phenyl benzyl ketone (0·5 g.) was treated with iodine (2·0 g.) and iodic acid (0·5 g.) in alcohol (50 ml.) at 60-70° with stirring and the reaction mixture was then left overnight and worked up as before.

7-Hydroxy-8-nitroisoflavone : Fuming nitric acid (1 ml.) in glacial acetic acid (4 ml.) was gradually added with stirring to a suspension of 7-hydroxyisoflavone (2·0 g.) in glacial acetic acid (15 ml.) externally cooled to 0°. The reaction mixture was kept overnight at room temperature and then poured over crushed ice. The product obtained crystallised from acetic acid in white needles (1·2 g.), m.p. 221°. (Found : C, 63·79 ; H, 2·64 ; N, 4·73. $C_{15}H_9NO_5$ requires C, 63·60 ; H, 3·18 ; N, 4·94%).

The methyl ether : Prepared by methylating the above nitro derivative with dimethyl sulphate in acetone solution in presence of anhydrous potassium carbonate and crystallised from acetic acid in colourless needles gave m.p.

219°. (Found : C, 64·64 ; H, 3·75 ; N, 4·72. $C_{16}H_{11}NO_5$ requires C, 64·65 ; H, 3·70 ; N, 4·71%).

2, 6-Di-phenylacetoxy nitrobenzene : 2-Nitroresorcinol (0·5 g.) was taken in sodium hydroxide (10 ml ; 10%) and phenyl acetyl chloride (1·2 g.) was added with stirring. The solid which separated was crystallised from alcohol in colourless plates (0·2 g.), m.p. 124°. (Found : C, 67·06; H, 4·42 ; N, 3·27. $C_{22}H_{17}NO_6$ requires C, 67·51 ; H, 4.35 ; N, 3·58%).

2, 4-Dihydroxy-3-nitrophenyl benzyl ketone : The above ester (2·0 g.) was taken in nitrobenzene (4 ml.) and anhydrous aluminium chloride (1 g.) in nitrobenzene was added. The reaction mixture was left overnight at room temperature and then heated at 70-80° for half an hour. The product obtained on working up as usual was crystallised from alcohol in pale yellow plates (1 g.), m.p. 109°. (Found : C, 61·6 ; H, 4·07 ; N, 5·21. $C_{14}H_{11}NO_5$ requires C, 61·53 ; H, 4·02 ; N, 5·13%).

The above ketone (2 g.) was refluxed with ethyl ortho formate (2·5 ml.) pyridine (4 ml.) and piperidine (0·5 ml) for 5 hr. The product obtained on pouring the reaction mixture in dilute hydrochloric acid was crystallised from acetic acid, m.p. 224°. Mixed m.p. with 7-hydroxy-8-nitroisoflavone described above was not depressed.

7-Hydroxy-4'-nitroisoflavone : 7-Hydroxyisoflavone (1·0 g.) was gradually added to a mixture of nitric acid (1·42 d. 0·2 ml.) and sulphuric acid (1 ml.) kept below 5°. The reaction mixture was kept for 1 hr. with occasional stirring and poured over ice cold water. The product obtained crystallised from acetic acid in colourless buds (0·5 g.), m.p. 290°. (Found : C, 63·71 ; H,2·90 ; N, 5·09. $C_{15}H_9NO_5$ requires C, 63·60 ; H, 3·18 ; N, 4·94%). Mixed m.p. with the product prepared according to Karmarkar[2] was not depressed.

The methyl ether : Prepared by methylating the above isoflavone and crystallised from acetic acid gave m.p. 248°. (Found : C, 64·99 ; H, 3·77 ; N, 4·59. $C_{16}H_{11}NO_5$ requires C, 64·65 ; H, 3·70 ; N, 4.71%).

The same compound was also prepared by adding 7-methoxyisoflavone (1 g.) to a mixture of nitric acid (1·42 d. ; 0·2 ml.) and sulphuric acid (1 ml.) at 0-5°. It was poured on ice after one hour and the product crystallised from acetic acid in colourless plates, m.p. 248°.

7-Hydroxy-8, 4'-dinitroisoflavone : 7-Hydroxyisoflavone (1 g.) was gradually added to a mixture of nitric acid (1·42 d. ; 2 ml.) and sulphuric acid (2 ml.) kept at 5-10° and the reaction mixture stirred for 2 hr. The product obtained on pouring the reaction mixture in water crystallised from acetic acid in pale yellow buds (0·8 g.), m.p. 265°. (Found : C, 55·19 ; H, 2·44 ; N, 8·22. $C_{15}H_8N_2O_7$ requires C, 54·88 ; H, 2·44 ; N, 8·53%).

The methyl ether : Prepared by methylating the above dinitroisoflavone with dimethyl sulphate in acetone solution in presence of anhydrous potassium carbonate. On crystallisation from dilute acetic acid in colourless needles gave m.p. 210°. (Found : C, 56·23 ; H, 3·19 ; N, 7·77. $C_{16}H_{10}N_2O_7$ requires C, 56.14; H, 2·92 ; N, 8·18%).

The same compound was also prepared by gradually adding 7-methoxyisoflavone (1 g.) to a mixture of nitric acid (1·42 d. ; 2 ml.) and sulphuric acid

(2. ml.) kept at 5-10°, stirring the reaction mixture for 2 hr and then pouring it in ice cold water.

Summary

7-Hydroxyisoflavone on bromination with different quantities of bromine gave the 8-bromo-, the 6, 8-dibromo and the 2, 6, 8-tribromo derivatives. Iodination of the same isoflavone with iodine and iodic acid or with iodine and ammonia gave the 8-iodo and the 6, 8-diiodo derivative. On nitration, 7-hydroxyisoflavone and its methyl ether gave the 8-nitro, the 4'-nitro and the 8, 4'-dinitro derivative under different conditions of nitration.

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HYDROGEN PEROXIDE OXIDATION OF SOME AROMATIC COMPOUNDS*

By

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Phenolic aminoacids are often the ultimate metabolites of aromatic or hydroaromatic steroid[1,2]. The study of these metabolites would be easier if they were labeled. Turner[3, 4] described methods for the labeling of C-3 position of non-aromatic steroids.

It was the objective of this study to devise a route to open and rebuild ring A of aromatic or hydroaromatic steroids. A C^{14} label can be introduced into the molecule at an appropriate position during the course of ring formation.

Such a route was found in the work of Fernholz on the action of peracetic acid on phenols or their ethers[5].

In recent years, Greenspan[6, 7] described the preparation of peracetic acid in better and higher yields. Greenspan used the reagent to oxidize ring A of either β-naphthol or its methyl ether.

Our main objective was to study the effect of peracetic acid on 7-methyl bisdehydrodoisynolic acid[8]. As preparatory experiments, however, we studied the action of the oxidant on β-naphthol, β-naphthol methyl ether, β-naphthylamine, anisole, and 7-methyl bisdehydrodoisynolic acid.

Depending on the experimental condition β-naphthol yielded a dimer of 1, 2-naphthoquinone, a mixture of cis- and trans-o-carboxy cinnamic acid which often changed to the lactone. β-naphthyl methyl ether yielded a mixture of o-carboxy cinnamic acids or their lactones, and a dimer of 1, 2-naphthoquinone.

Peracetic acid oxidation of β-naphthylamine yielded a neutral substance of melting point 279·7° which was not further studied.

Oxidation of anisole produced a mixture of cis- and transmuconic acids which were not studied thoroughly, either.

Attempts to oxidize β-naphthol or its methyl ether in presence of 85% potassium hydroxide or pyridine and hydrogen peroxide failed to yield any acidic material.

Only tarry products were obtained if peracetic acid reacted for a considerable length of time on either β-naphthol or its methyl ether.

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* This work was completed in 1956.

In connection with the oxidation of β-naphthol or its methyl ether with peracetic acid the effect of two solvents was studied. Such solvents were: chloroform and cyclohexane. Reaction mixtures containing chloroform as the solvent was homogeneous and those containing cyclohexane, heterogeneous. In case a substance was more soluble in cyclohexane than in chloroform a mixed cyclohexane—chloroform (10:1) solvent was found useful to give a homogeneous reaction mixture.

In preparing peracetic acid same volume of 70% perchloric acid was used, in some experiments, in place of concentrated sulfuric acid as the catalyst. The effect of peracetic acid reagent thus formed was studied on the oxidation of β-naphthol. The color of reaction mixtures was greenish rather than the usual light brown and also more tar was formed. Perhaps, lesser amounts of perchloric acid could substitute sulfuric acid as a catalyst in the preparation of peracetic caid. This point was not studied any further.

Studies on the oxidation of 7-methyl bisdehydrodoisynolic acid were complicated by the presence of a carboxyl group in the starting material. However, both the starting acid and its methyl ester were oxidized. Cinnamic acid derivatives were obtained as oxidation products which were isolated as geometrical isomers or as their lactones.

Experimental

Lactone of o-carboxycinnamic acid from Nerolin

This oxidation was based on the work of Greenspan[7] and Fernholz[5]. Ice cold peracetic acid reagent[7] from 2·3 ml. (0·04 mole) acetic acid ; 0·7 ml. (0·026 mole) 90% hydrogen peroxide[9] 10 μl (0·0001 mole) sulfuric acid and 3·8 ml. (0·04 mole) acetic anhydride was cautiously added, with swirling, over a period of about ten minutes to a solution of 1·12 g. (0·007 mole) of β-naphthol methyl ether[10], mp. 70-71°, in 15 ml. of chloroform at ice water temperature. After one day at room temperature the dark brown solution was taken up with 100 ml. of ether and 50 ml. of ethyl acetate and washed in succession with water, freshly prepared aqueous 1% ferrous sulfate solution slightly acidified with sulfuric acid until the washings did not turn orange, water, saturated brine, and dried with magnesium sulfate. Evaporation of the solvents on the steam bath under a stream of nitrogen gave a gummy solid. Lactone test[11] was positive and anydride test[11] negative. The gummy solid was taken up in 100 ml. ether and washed with saturated sodium bicarbonate solution and water. After drying with magnesium sulfate and evaporating the solvent there was obtained 0·2234 g. of neutral material (19·9%) solid, mp. 61-65°. Crystallization from dilute alcohol gave 0·203 g. (18%), mp. 69-71° of solid which on admixture did not depress the mp. of authentic nerolin.

The bicarbonate layer was acidified with hydrochloric acid and the organic material was taken up in ethyl acetate-ether. After washing the extract with water, saturated brine, drying over magnesium sulphate and removal of the solvent yielded 1·93 g. of crude acidic[12] material, mp. 127-143° and 76%

yield. The lactone test[11] was positive while the anhydride test[11] and ferric chloride tests were negative.

Phthalide Acetic Acid—Lactonizaton

Crude o-carboxy cinnamic acid, mp. 188-190°, 138 mg., lactone-free, was refluxed for about 20-21 hours with 20 ml. 25% hydrochloric acid and 20 ml. acetic acid. The cold reaction mixture was diluted with 50 ml. water and the organic material was taken up with a mixture of ether and ethyl acetate. The extract was washed in succession with water and saturated brine. After drying with magnesium sulfate and removing the solvents on the steam bath in a stream of nitrogen there was obtained 0·198 g, 74% based on nerolin, mp. 125-135°, of a solid which after two crystallizations from a mixture of acetone and benzene (1 : 3) yielded 0·1169 g. (43% based on nerolin) of colorless solid rosettes, mp. 147·4-149·5°[14] The mp. was unchanged on admixture with authentic lactone (see below).

O-carboxycinnamic Acid

1·03 g. (0·00536 mole) sample of crude acid, mp. 127-143°, was dissolved in 25 ml. of 5% aqueous potassium hydroxide[12] and warmed on a steam bath for one hour. The solution was diluted with 25 ml. of water, cooled, filtered and acidified to pH 4 with 6 ml. acetic acid in the cold. The organic material was extracted with a mixture of ether and ethyl acetate and then washed with water until neural, and dried over magnesium sulfate. Evaporation of the solvent gave 0·9598 g. (93%) of slightly colored solid, mp. 130-145°, which was negative to the lactone test[11]. Three crystallizations from a minimum of 95% acetone gave 0·1859 g. (23% yield) of stout rods with a constant[15] mp. 192·9-194·8° and a negative lactone test.

For analysis a small portion, 0·0019 g. was sublimed rapidly at 160-165° (0·03 mm.) of Hg., to obtain a solid, mp. 192·9-194·1°, lactone test negative. *Anal* Calcd. for $C_{10}H_8O_4$: C, 62·5 ; H, 4·0. Found : C, 63·10 H, 4·5.

Alc λmax.	221 mμ	270 mμ (logE 4·37, 4·30)
Alc λmin.	244 mμ	(logE 4·08)

The mother liquors yielded after repeated crystallization 0·1614 g. of material (15·7%) of mp. 191·8-192·9°, lactone test negative.

Saponification of Lactone of O-Carboxycinnamic Acid

The lactone of o-carboxycinnamic acid 0·0088 g. (0·0458 mole), mp. 147·4-149·5° was dissolved in 5 ml. of 5% aqueous sodium hydroxide and warmed on a steam bath for one hour. The solution was cooled, acidified with 6 ml.

of acetic acid containing a drop of hydrochloric acid to pH 2. The organic material was taken up in ether and ethyl acetate, and the extract was washed with water until negative to silver nitrate test for chloride ion, dried over magnesium sulfate and the solvent was removed. The residue was crystallized once from 95% acetone, yield 0·0078 g. (89%) of short rods, mp. 188·7-190·0°.

Phthalide free from Acid Anhyrdide

The preparative method[16] for phthalide was modified to eliminate the yellow impurity. After lactonization, a product was obtained of mp. 60-73° which was positive to the anhydride test[11] and nitrogen test[17]. After sublimation of 0·180 g. at 130° and 43 mm. of Hg. 0·1365 g. of material, mp. 60-63° and positive to the anydride test but negative to the nitrogen test was obtained. Further sublimation at 180-190° and 43 mm. of Hg. gave 0·0150 g. of material mp. 90-110° which was positive to the nitrogen test.[17]

This material was refluxed with 10 ml. of Feigl's[11] anhydride reagent and evaporated to dryness. The organic material was taken up in ethyl acetate, the extract was washed with water and then saturated brine and dried over magnesium sulfate. After evaporating the solvent there remained 0·0752 g. of solid, mp. 60-62° negative to the anhydride test.[11] Three crystallizations from dilute ethanol and sublimation at 120° (44 mm. of Hg.) gave 0·0742 g. mp. 68-69° negative to tests for nitrogen and anhydride.

Alcohol			
λmax.	227	274	281 mμ
logE	4·05	3·25	3·24
Alcohol			
λmin.	250	278 mμ	
logE	2·62	3·18	

Ozonization of O-Carboxycinnamic Acid : Formation of Phthalide :

166·8 mg. of the bicarbonate extractable material from the oxidation of nerolin were dissolved in a solvent mixture of 20 ml. ethyl acetate and 20 ml. acetic acid. Passed ozonized oxygen for 15 mins., decomposed with 10 g. zinc and 30 ml. water overnight in the cold room. Added a few drops of HCl, extracted with ether, dried, and removed solvent to yield 67·9 mg. of material, mp. 67-8°. After three recrystallizations from dilute alcohol (cold) and a final sublimation at 110-12° (43 mm.) mp. was 69-71°.

Found	C—71·88	H—4·9
$C_8H_6O_2$ requires	C—71·6	H—4·5

Diazomethane Esterification of Beta-Naphthol Oxdaton Product

[illegible] mg. of a bicarbonate extractable material, mp. 175-179°, were treated [illegible] with diazomethane from 0·5 g. nitrosomethylnitro-

guanidine, washed with water, dilute alkali, water, dried, solvent removed and sublimed to yield 124·7 mg. of a mobile yellow liquid, twice resublimed and analyzed.

Found	C—65·13	H—5·46
$C_{12}H_{12}O_4$ requires	C—65·44	H—5·45

Peracetic Oxidation of Beta-Naphthol : Dimer of 1, 2-Naphthoquinone :[18]

Two grams (0·014 mole) of beta-naphthol, mp. 120-122°, in 9 ml. glacial acetic acid were added at room temperature to 7·5 ml. peracetic reagent containing 1·15 g. (0·03 mole) hydrogen peroxide. Each drop of the light red colored solution of naphthol decolorized on addition to the peracetic acid reagent. With half of the naphthol solution added the color turned light carmin. Towards the end of the addition process the color turned dark-brown. After about sixty-six hours at room temperature the solution was diluted with 30 milli-liters of water when a brown semi-solid mass separated. Yield obtained was 1·8 g. (64%) of a crude substance, mp. 155-166°, after drying. This substance was sparingly soluble in acetone, ether, water containing drops of HCl, alcohol, benzene, water, acetic acid, butyl acetate, ethyl acetate, cyclohexane, n-hexane, and methanol but readily soluble in dioxane.

After several crystallizations from dioxane-methanol it had a melting point of 276·6-277·1° (corr).

Analysis	C—76·0	H—3·8
$C_{20}H_{10}O_4$ requires	C—76·4	H—3·2

This substance reduced aqueous permanganate and was insoluble in sodium bicarbonate solution.

Preparation of β-naphthyl methyl ether : 20 g. beta naphthol, 26 ml. methanol, and 4 ml. concentrated sulfuric acid yielded 19 g. of the ether, mp. 70-71.[19]

Peracetic Acid Oxidation of Beta-Naphthylamine

One gram (0·007 mole) of beta-naphthylamine, mp. 108-110°, in 4·5 ml. acetic acid was treated at room temperature with 3·75 ml. peracetic reagent containing 0·575 g. (0·015 mole) of hydrogen peroxide. During addition of the reagent effervescence took place. After 18-20 hours at room temperature the reaction mixture was extracted with saturated sodium bicarbonate solution and 5% sodium hydroxide solution. The alkaline solutions were extracted with ether and n-butyl acetate. The organic layers were washed with water, dried and evaporated to dryness under nitrogen.

The residual substance from the neutral fraction which was a greenish lustrous substance had crude melting point 279·7°. The substance was sparingly soluble in acids, alkalis, ether, benzene, ethyl acetate, hexane, cyclohexane, chloroform and moderately soluble in butyl acetate and chloroform.

The alkaline layers were acidified and extracted with ether. The ether layers were washed with water, dried and evaporated to dryness under nitrogen. The residue appeared to be the same as that obtained from the preceding ether extraction.

Peracetic Oxidation of Anisole

One gram (0.009 mole) of anisole in 5 ml of chloroform was treated at room temperature with 3·75 ml peracetic reagent (1·575 g; 0·015 mole). The reaction in chloroform was rather sluggish and required warming up to get a clear solution from an oily emulsion. The warming was continued for 15 minutes till the solution became carmine red. The reaction mixture was left at room temperature for 16 hours, washed with water, dried and evaporated to dryness to obtain a small amount of solid, melting point—crude 117-130°. This was obviously a mixture of cis—and trans muconic acids. This mixture was not studied further.

Tribasic Acid

7-Methyl bisdehydrodoisynolic acid (13), mp 225-227° (corr.) (508·2 mg., 1·7 m mole) in chloroform (30 ml) was treated with 1·1 ml peracetic acid reagent[7] every day for fifteen days. In fifteen days 16·5 ml of the oxidant was added.

The chloroform solution upon addition of the oxidant turned light yellow which changed to dark orange in course of the reaction. Upon completion of the reaction period of fifteen days the mixture was diluted with 100 ml of ether which was washed in succession with water, freshly prepared ferrous sulfate solution (1%) containing traces of sulfuric acid. The ferrous sulfate washings were now washed throughly with water, dried and the solvent removed. A glass 0·6279 g (111%), was left behind. Lactone and anhydride tested were found negative.

The glass was now warmed on a steambath for an hour with 10 ml of 5% KOH solution (tested alkaline with indicater paper), diluted with 10 ml of H_2O, filtered, added 2 ml of acetic acid (acidic by indicator paper). The separated white solids were extracted with ether, washed with water, dried and solvent removed. Yield 569·8 mg, lactone test negative. This was sublimed at 180-190° (0·03 mm) Fr. 1., 39·4 mg—crystallized from acetone, mp—and mixed mp was that of the starting material Fr. II. up to 250° (0·03 mm), 147·3 mg of a glass with solids, mp 225-29°, lactone test negative. This was crystallized to constant mp from benzene acetone cyclohexane (1 : 1 : 1), Wt. 302·6 mg (53·3% of theory), needles, mp 248·7-251·9°, same mp as that of the analytical sample. Lactone and anhydride tests were negative.

Analysis: $C_{17}H_{12}O_6$ req. C - 65·06; H-6·02, Found C-65·13; H-6·13. Products from two other batches of preparation had the following analyses: C—64·86, 65·06; H- 6·31, 6·07.

The ultraviolet spectrum of the first analyzed sample had the following characteristics :

Alcohol					
λMax	243·5	276·5	286	320	335mμ
LogE	4·23	3·23	3·22	1·76	1·68
Alcohol					
λMin.	226	268	282	315	331mμ
LogE	3·95	3·12	3·18	1·75	1·66

Trimethylester of Tribasic Acid

A solution of 0·0017 g (0·0005 mole) of tribasic acid, mp 248·7 – 251·9°, in 75 ml of ether was treated with an etheral solution of excess of diazomethane. The solvent was evaporated and the residue was washed with cold methanol, acetone, and methanol-ether mixture and sublimed at 180-190° (0·03 mm) (43%) of needles, mp 173·3-175·3°, with previous softening at 155·7-157·1°.

Found : C, 67·12; H, 6·83

From another batch of preparation the ester was obtained in 39% yield. Calcd. for $C_{21}H_{26}O$ req. C—67·37 H—6·95 Found C—66·98; H—6·53.

Alcohol				
λMax	242	277	286	334 mμ
LogE	4·31	3·28	3·26	1·62
Alcohol				
λMin	224	265	282	331·5 mμ
LogE	4·0	3·17	3·22	1·59

A Second Isomer of Tribasic Acid

In several preliminary experiments directed towards the preparation of the tribasic acid the chloroform extract was washed with saturated sodium bicarbonate solution previous to the ferrous sulfate wash (see above). The solvent was evaporated from the apparent neutral fraction and a residual gum was obtained. After repeated crystallization from benzene—cyclohexane there was obtained long needles of mp 150·5—152·5° which were negative to the lactone test[1]. Anal. Calcd. for $C_{18}H_{20}O_6$: C, 65·06 ; H, 6·02%.

Found : C—65·88; H, 6·85

Alcohol			
λMax.	245	276·5	286 mμ
LogE	4·26	3·2	3·18
Alcohol			
λMin.	226	269	282 mμ
LogE	3·92	3·12	3·15

Isomerization of Lower Melting Acid to Higher Melting Tribasic Acid

A solution of 0·0029 g (0·007 m mole) of tribasic acid, mp 150·5 – 152·5°, in 0·5 ml of 5% aqueous potassium hydroxide and 1·5 ml of 95% ethanol was refluxed for two hours. The alcohol was evaporated under reduced pressure and the aqueous solution was cooled and acidified with 150 μl of acetic acid. The organic material was taken up in ether, washed with water, saturated brine and then dried over magnesium sulfate. After evaporating the solvent, subliming at 245° (0·04 mm of Hg) and two crystallizations from acetone-cyclohexane (1 : 1) the mp was 244·1-249·7° on admixture with authentic tribasic acid of mp 248·7-251·9°, the mixed mp was 245·6-249·7°.

Effect of Alkali on Higher Melting Tribasic Acid

When an attempt was made to isomerize the acid of mp 249·7-251·8° by refluxing with 5% aqueous potassium hydroxide the unchanged starting material was recovered as was found by a mixed mp determination. This study indicated that the lower melting acid was the cis and the higher melting acid was the stable trans isomer.

Mono Esterification of Tribasic Acid

A solution of 0·0364 g (0·11 m mole) of tribasic acid, mp 244·5-247·7 in 5 ml of methanol and 5 ml of concentrated sulfuric acid was refluxed fourteen hours. After just neutralizing with barium carbonate the alcohol was removed under reduced pressure and the solution was acidified with acetic acid. The organic material was taken up in ether, washed with water, saturated brine, dried over magnesium sulfate and the solvent evaporated. The residue was sublimed at 195-200° (0·03 mm) crystallized from acetone—cyclohexane, dissolved in hexane—benzene (50%) and placed on an anhydrous magnesium sulfate column. The benzene eluate, weighed 0·013 g (39·5%), mp 193·9 – 204·2°. Repeated crystallization from acetone—cyclohexane gave material, mp 196 – 199·1°.

Anal. Calcd. for $C_{19}H_{22}O_6$: C, 65·8; H, 6·4.

Found: C, 65·6; H, 7·0.

Alcohol λMax.	245	277	286	335 mμ
LogE	4·44	3·46	3·47	2·85
Alcohol λMin	226	274	283	330 mμ
LogE	4·13	3·44	3·43	2·75

Lactonization of Tribasic Acid

All attempts to lactonize the tribasic acid by the procedure used successfully for the lactonization of o-carboxycinnamic acid failed. Only starting material was recovered unchanged.

Summary

The effect of peracetic acid has been studied on β-naphthylamine, anisole, and 7-methyl bisdehydrodoisynolic acid. Corresponding cinnamic acid derivatives or their lactones were the products. β-naphthylamine yielded a neutral compound which could not be identified.

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SPECTROPHOTOMETRIC STUDIES ON THE COMPOSITION AND STABILITY OF THE COMPLEX BETWEEN 3 : 5 DINITROSALICYLIC ACID AND Fe^{3+} IONS IN AQUEOUS MEDIUM

By

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Srivastava *et al*[1, 2] studied the reaction of titanium and tungsten with 3 : 5 dinitrosalicylic acid. We have seen that Fe^{3+} ions also react with this acid and form a water-soluble orange coloured complex. As no data are available in literature regarding the composition and stability of Fe- 3 : 5 dinitrosalicylic acid complex, this investigation gives the results obtained in such a study.

Experimental

3 : 5 Dinitrosalicylic acid was B.D.H., L.R. sample and was recrystallised before use. A pure solution of ferric chloride was prepared from ferrous ammonium sulphate[3] (B.D.H., A.R.) and the iron content was estimated by oxide method before preparing the standard solution. Potassium chloride (B.D.H., A.R.) was used for adjusting the ionic strength. Sodium acetate, hydrochloric acid and sodium hydroxide used were of B.D.H. A.R. quality.

Absorbance measurements were made by Hilger Uvispek spectrophotometer (Model H 700-308 of Hilger Watts Ltd., London) using one cm. effective light path. The cell compartment was fitted with jacket through which water could be circulated from a thermostat (Townson and Mercer Ltd. England). A thermometer inserted into the cell compartment and allowed to come to temperature equilibrium showed a variation of less than 0·5°C over a period of time much longer than those needed to make measurements of optical density.

Conductometric measurements were made using conductivity meter (LBR of Wissenschaftlich Technische Werkstatten, Germany). The titrations were carried out in a titration cell (type LTI) which had a thermostatic jacket for temperature stability. The pH measurements were made by Beckman pH meter (Model H2). All the solutions and subsequent dilutions were made with conductivity water.

Results and Discussion

(1) *Spectral studies* :—3 : 5 dinitrosalicylic acid ($M \times 10^{-3}$) and ferric chloride solution ($M \times 10^{-3}$) were taken in the ratio of 1 : 1, 1 : 2 and 1 : 3. Suitable

quantities of 1·0 M sodium acetate and 1·0 M HCl solutions were added and absorption were recorded at different wavelengths. The complex showed the maximum absorption at 450 mμ in all the cases, thus indicating the formation of the complex.[4] The absorbance due to 3:5 dinitrosalicylic acid and ferric chloride is very small at this wavelength. The corresponding wavelength of 450 mμ was thus used for subsequent work.

(ii) *Effect of pH* :—Solutions containing the same concentration of 3:5 dinitrosalicylic acid and ferric chloride were prepared at different pH values and absorbance noted at 450 mμ. It was found that the complex was stable between the pH range 2·7 to 3·2 and hence a pH of 3·0 was selected for subsequent studies.

(iii) *Effect of temperature* :—Mixtures were heated on water bath to 85°C, cooled to room temperature and absorbance was measured after making up the volume. There was no difference in the absorption of the sample and that prepared at room temperature. The complex was stable over a wide range of temperature variations.

Composition of the complex :

(i) *Job's method of continued variation* :—A series of solutions was prepared from 10^{-3}M ferric chloride and the acid in which the ratio of ferric to *acid* varied from 1:9 to 9:1. The pH was kept at 3.0 by the addition of

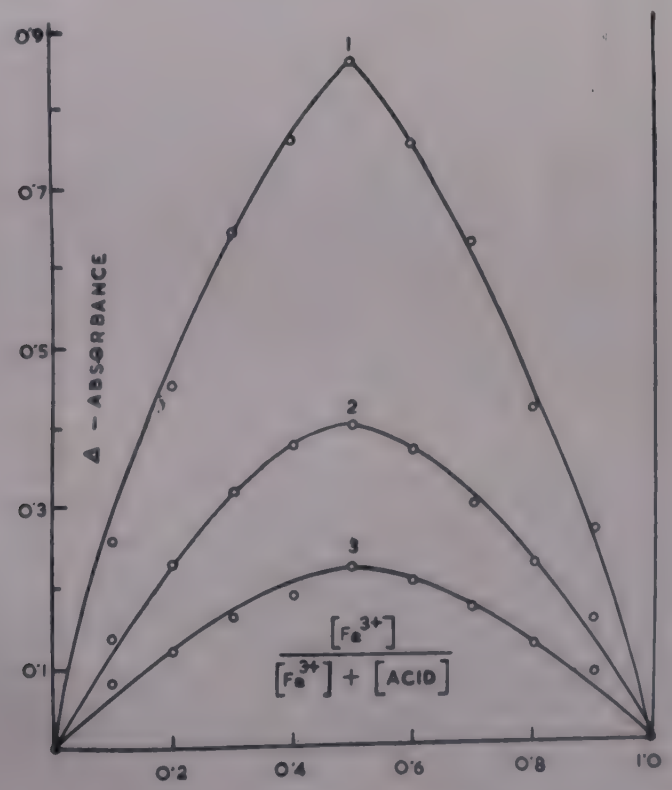


FIG. 1

Job's method of continued variation.
Curve 1. Total Molarity $1{\cdot}0 \times 10^{-3}$M.
Curve 2. Total Molarity $5{\cdot}0 \times 10^{-4}$M.
Curve 3. Total Molarity $2{\cdot}5 \times 10^{-4}$M.

suitable quantities of sodium acetate and hydrochloric acid. The difference of absorbance was plotted against the ratio $[Fe^{3+}]/[Fe^{3+}]+[Acid]$. Curves 1, 2 and 3 Fig. 1 were obtained using total molarity of 1×10^{-3}M, $5{\cdot}0\times10^{-4}$M and $2{\cdot}5\times10^{-4}$M respectively. The maximum at 0·5 in all the cases indicates the formation of the complex containing ferric and the acid in the ratio 1 : 1.

(ii) *Slope ratio method* :—The concentration of variable component was varied from $2{\cdot}5\times10^{-5}$M to $1{\cdot}5\times10^{-4}$M in presence of excess concentration of 1×10^{-3}M of the constant component (curves 1 and 2 Fig. 2). The pH of solutions was maintained at 3·0. The difference of absorbance at 450 mμ was plotted against the concentration of variable component. The slopes of two straight lines proved the ratio of the ferric and acid as 1 : 1. The same ratio is also obtained by varying the concentration of variable component from $1{\cdot}25\times10^{-5}$M to $7{\cdot}5\times10^{-5}$M in presence of excess concentration of $0{\cdot}5\times10^{-3}$M of constant component. (Curves 3 and 4 Fig. 2).

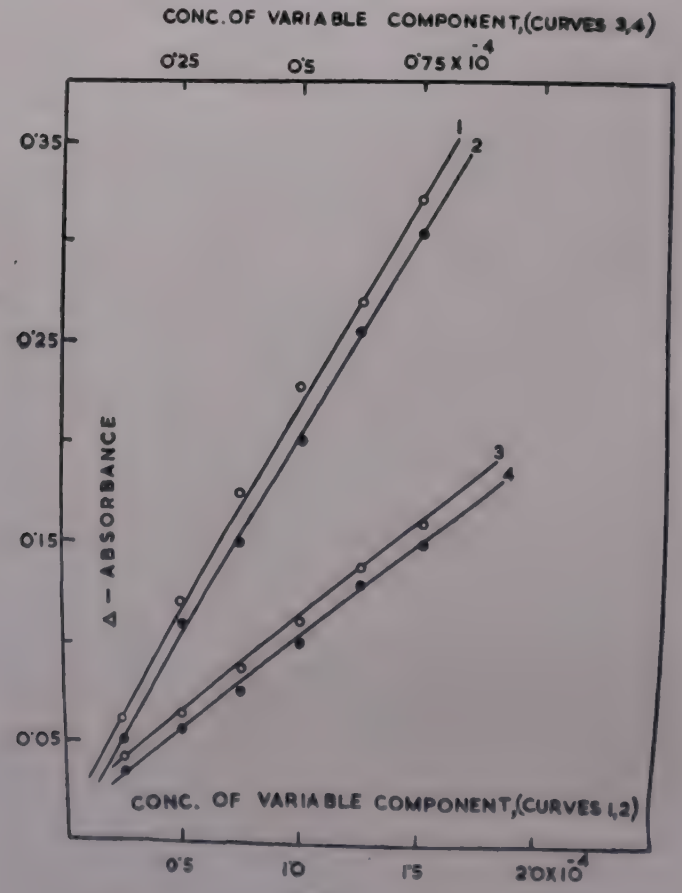


FIG. 2

Slope ratio method.
Curves 1 & 3. Fe^{3+} varying.
Curves 2 & 4. Reagent varying.

(iii) *Molar ratio Method* :—A series of solutions was prepared from $5{\cdot}0\times10^{-4}$M and $2{\cdot}5\times10^{-4}$M of the acid at pH 3·0 as described earlier and varying amounts of ferric solution were added so that the mole ratio of acid

to ferric was from 1 : 0·2 to 1 : 7. Curves 1 and 2 Fig. 3 show breaks at a ratio of one mole of acid to one mole of ferric ion.

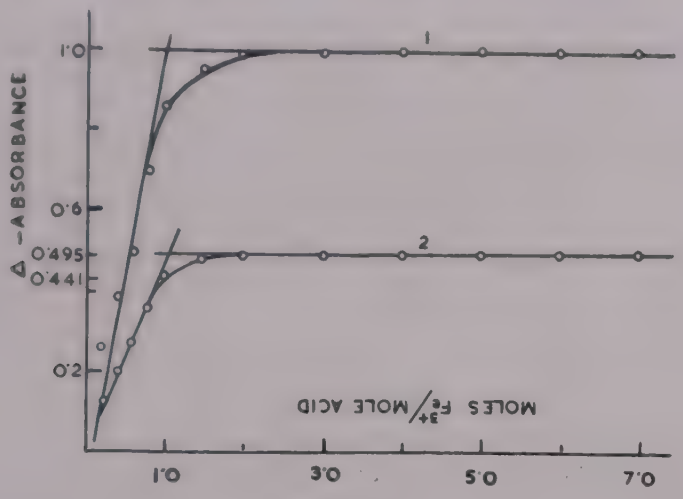


FIG. 3

Molar ratio method.
Curve 1. $5{\cdot}0\times10^{-4}$M concn.
Curve 2. $2{\cdot}5\times10^{-4}$M concn.

Molecular extinction coefficient and instability constant :

Using optical densities of solutions containing large excess of acid so that as a first approximation the concentration of the complex may be taken to be equal to that of ferric ions added, the molecular extinction coefficient of the complex is found to be $2{\cdot}106\times10^{3}$. The instability constant of the complex

$$K=\frac{\{[Fe^{3+}]\ \text{Total}\ -[\text{Complex}]\}\ \{[\text{Acid}]\text{Total}\ -[\text{Complex}]\}}{[\text{Complex}]}$$

has been calculated where the concentration of the complex is obtained from the extinction coefficient of the complex. The instability constants of the complex at pH 3·0 have been determined at ionic strengths 0·01, 0·02, 0·05, 0·08, 0·10, 0·15 and 0·20 (Table 1).

TABLE 1

Effect of ionic strength on the instability constant of the complex between Fe^{3+} ion and 3:5 Dinitrosalicylic acid in aqueous medium

pH = 3·0; λ = 450 mμ; Temp. = 30°C.

Ionic strength (I)	Instability constant
0·01	$3{\cdot}77\times10^{-6}$
0·02	$5{\cdot}76\times10^{-6}$
0·05	$8{\cdot}49\times10^{-6}$
0·08	$1{\cdot}13\times10^{-5}$
0·10	$1{\cdot}46\times10^{-5}$
0·15	$2{\cdot}18\times10^{-5}$
0·20	$3{\cdot}00\times10^{-5}$

The instability constant of the complex at a constant ionic strength of 0·01 has also been determined at different temperatures. The results are recorded in Table II. Further, the logarithms of the instability constant have been plotted against 1/T (Fig. 4). From the slope of the straight line, ΔH has been found to be $-7{\cdot}384$ k.cals. Assuming this to be constant over the range of experimental temperatures, ΔS of the reaction has also been calculated and is 49·17 e.u.

TABLE 2

Instability constant of the complex at different temperatures

Ionic strength = 0·01; pH = 3·0; $\lambda = 450$ mμ

Temp. °K	Instability constant
293·16	$4{\cdot}84 \times 10^{-6}$
303·16	$3{\cdot}77 \times 10^{-6}$
313·16	$2{\cdot}67 \times 10^{-6}$
323·16	$1{\cdot}87 \times 10^{-6}$
333·16	$1{\cdot}25 \times 10^{-6}$

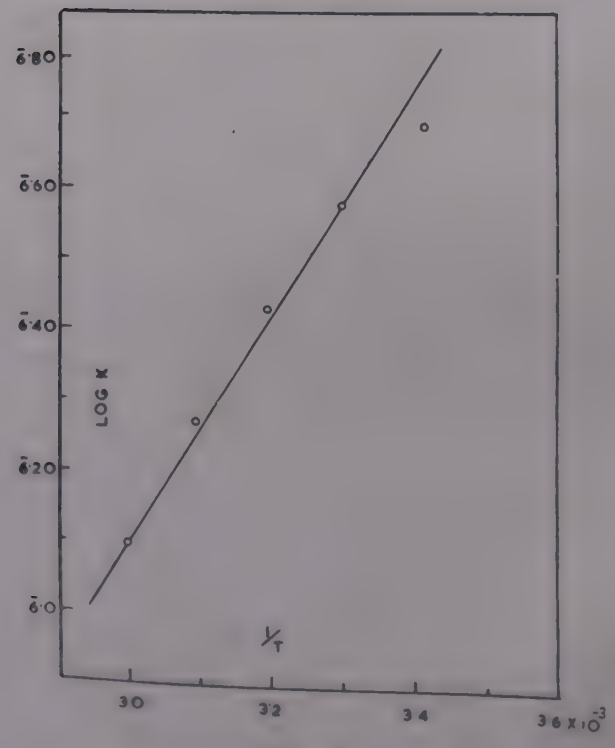


FIG. 4
Variation of log K with 1/T.

Attempt has also been made to calculate instability constant by molar ratio method. The dissociation of the complex may be written as

$FeR \rightleftharpoons$	Fe^{3+}	$+ R^-$	
C	O	O	Initial concentration.
$C(1-\alpha)$	αC	αC	Final concentration.

where C is the concentration of the complex and α is the degree of dissociation. The instability constant K is given by the equation—

$$K = \frac{\alpha C \times \alpha C}{(1-\alpha)C} = \frac{\alpha^2 C}{(1-\alpha)}$$

From curve 2, Fig. 3—

$$\alpha = \frac{E_m - E_s}{E_m} = \frac{0{\cdot}495 - 0{\cdot}441}{0{\cdot}495} = 0{\cdot}110$$

where the terms have their usual significance. Since the concentration of the complex is $2{\cdot}5 \times 10^{-4}$M, by substituting these values in the above equation the value of K at 30°C comes to $4{\cdot}11 \times 10^{-6}$.

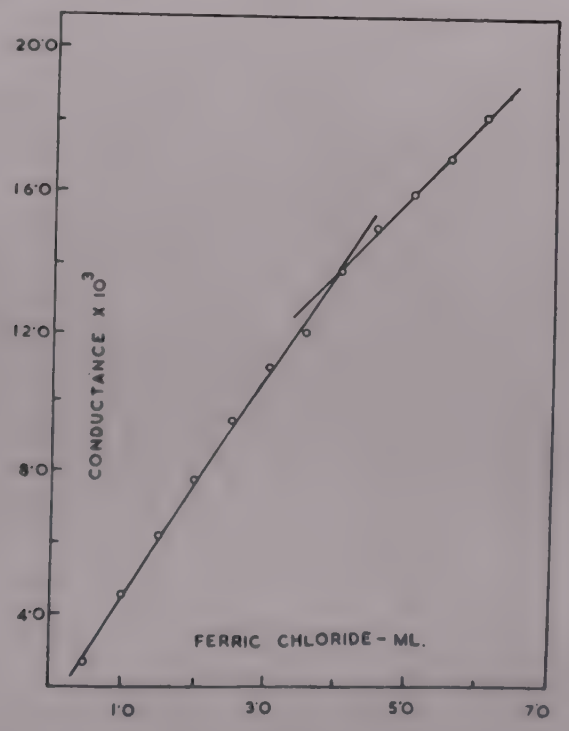
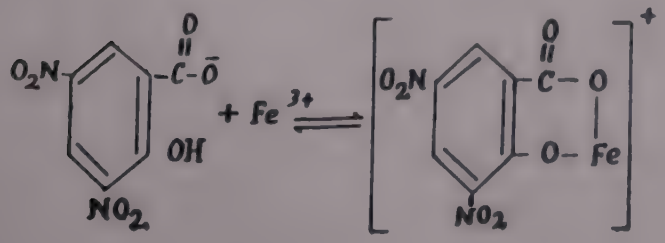


FIG. 5

Conductivity method.
40 ml. of $1{\cdot}0 \times 10^{-3}$M acid VS.
$1{\cdot}0 \times 10^{-2}$M ferric chloride solution.



Conductometric studies:—The composition of the complex is also confirmed by conductometric measurements. Fig. 5 shows the titration curve of 40 ml. of 1×10^{-3}M of the reagent against 1×10^{-2}M solution of ferric chloride. The break indicates the ratio of reagent to ferric ion as 1 : 1. The probable structure of the chelate may be as follows :

Summary

The composition of orange coloured water soluble complex formed by 3 : 5 dinitrosalicylic acid with Fe^{3+} ion has been studied by Job's method of continued variation, slope ratio method and molar ratio method spectrophotometrically. The colour produced is almost instantaneous and stable towards time. It has an absorption maximum at 450 mμ. The optimum pH range is 2·7 to 3·2. The molecular extinction coefficient of the complex is $2{\cdot}106 \times 10^3$. The instability constant of the complex has been given for different ionic strangths and at different temperatures. The values Δ H and Δ S are found to be −7·384 k. cals. and 49·17 e.u. respectively.

Acknowledgement

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FIXATION OF POTASSIUM IN BIHAR SOILS

By

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In a previous paper the authors[11] showed that there were large variations in the potassium fixation capacity of Bihar soils. The potassium fixation was related to the nature of clay minerals in soils and higher fixation values were associated with illitic clays. The K fixation which is a dynamic property of the soils, depends primarily on the moisture conditions and management practices of soils. In tropical conditions, such as ours, the land undergoes intense wetting and drying processes, one following the other, causing varying degrees of K fixation in soil. The use of inorganic fertilisers with or without organic manure, and liming the acid soils in course of their reclamation may bring about a difference in the availability of K which is related to the phenomenon of K fixation in soils. The objective of the present study was, therefore, to asses the effects of various factors, such as wetting and drying, addition of large amounts of potassium or calcium to the soils and removal of organic matter from the soil on the extent of K fixation.

Experimental

The same 14 soil samples as used in a perevious study by the authors[11] representing sedentary and alluvial soils of Bihar were used in the present investigation. The K fixation studies were made in four series of experiments. In the first series, the fixation due to alternate wetting and drying was determined in accordance with the method suggested by Volk.[14] The method consisted of treating 10 g. soils with 10 mg. of K_2O in 10 ml. of KCl solution and wetting and drying 10 times on a steam plate followed by leaching with neutral normal ammonium acetate solution. Second series of experiments involved the treatment of 10 g. soils with 10, 25, and 50 mg. K_2O in ml. of KCl solution, while in the third series 10 g. soil were equilibrated for 72 hours with 20 mg. of Ca as 10 ml. of calcium hydroxide solution before treatment with KCl solution. In the fourth series, organic matter was removed from 10 g. soils with excess of hydrogen peroxide or bromine water followed by treatment with KCl solution. In the second, third and fourth series of experiments, wet method of fixation was followed as recommended by Schffelen and van der Marel.[13] The procedure consisted of leaching the soils, previously treated with KCl solution.

with 0·5N magnesium acetate solution. In all the cases exchangeable K of the check soil was determined. A flame photometer was used for the estimation of K throughout. K fixed was computed as follows: K added *minus* (exchangeable K for treated soil *minus* exchangeable K for check soil).

Results and Discussions

Effect of alternate wetting and drying of soils:—The effects of alternate wetting and drying treatments were variable in different soils as may be evident from Table 1.

TABLE 1

Potassium Fixation on Alternate Wetting and Drying of Soils

Soils	Percent fixation		% increase
	Before treatment	After treatment	
Chaibasa ...	12·64	46·80	270·2
Putida ...	39·75	69·90	75·9
Ranchi ...	−6·64	25·00	476·5
Giridih ...	29·71	62·50	110·3
Hazaribagh ...	17·66	25·00	41·7
Gaya ...	29·71	56·25	93·6
Nawadah ...	29·71	60·93	105·1
Bikramganj ...	25·67	46·87	82·6
Patna ...	47·78	58·88	23·2
Sabour ...	23·68	81·25	243·4
Katihar ...	26·02	56·25	116·1
Araria ...	18·66	62·50	234·9
Saharsa ...	43·76	75·10	71·6
Raxaul ...	43·76	62·50	42·9

Large variations in the increase of K fixation (23 to 476%) was observed on subjecting the soil to alternate wetting and drying treatment. Increase in fixation was very high (>200%) in the soils of Ranchi, Chaibasa, Araria and Sabour. Intermediate degree of increase (100 to 200%) was recorded in Giridih, Nawadah and Katihar soils. The remaining soils showed relatively lower degrees of fixation (<100%). Similar variations in K fixation have been reported by Volk,[11] Chaminade[1] and Richard and McLean,[12] on the soils studied by them.

The high fixation in Sabour and Araria soils is undoubtedly due to the preponderance of illites and also the presence of muscovites in considerable quantities. The findings of Mitra *et al.*[9] are in agreement with the above observation. The higher initial levels of potassium in North Bihar soils might cause large fixation. The high fixation of Ranchi and Chaibasa soils is not properly understood, as they do not contain any considerable amount of muscovite, and kaolinites are more preponderant than illites.

Effect of varying concentrations of potassium:—Effects of treatments of soils with 100, 250, and 500 mg. K_2O per 100 g. soils or 2,000, 5000 and 10,000

pounds of K_2O per acre respectively, on fixation of potassium are shown in Table 2.

TABLE 2
Potassium Fixation with Varying Concetrations of K

Soils	K_2O treatment per 100 g. soils					
	100 mg.		250 mg.		500 mg.	
	mg. of K_2O fixed	% fixation	mg. of K_2O fixed	% fixation	mg. of K_2O fixed	% fixation
Chaibasa ...	12·64	12·64	52·27	20·91	58·70	11·74
Putida ...	39·75	39·75	155·90	62·36	160·20	32·04
Ranchi ...	−6·64	−6·64	59·30	23·72	65·75	13·15
Giridih ...	29·71	29·71	57·27	22·91	68·90	13·78
Hazaribagh ...	17·66	17·66	62·75	25·10	70·75	14·15
Gaya ...	29·71	29·71	65·40	26·16	72·80	14·56
Nawadah ...	29·71	29·71	54·77	21·91	63·75	12·75
Bikramganj ...	25·66	25·66	73·40	29·36	70·75	14·15
Patna ...	47·78	47·78	115·60	46·24	119·65	23·93
Sabour ...	23·68	23·68	65·25	26·10	68·90	13·78
Katihar ...	26·02	26·02	95·40	38·16	109·60	21·92
Araria ...	18·66	18·66	93·40	37·36	107·55	21·55
Saharsa ...	43·76	43·76	52·77	21·11	68·75	13·75
Raxaul ...	43·76	43·76	87·32	34·93	109·60	21·92

It may be observed that with the increase in the concentration of K in solution the amount of K fixed also increased quantitatively. The intermediate dose (250 mg.%) appeared to have caused higher % fixation than the lower dose in a number of soils, e.g., soils of Chaibasa, Putida, Ranchi, Hazaribagh, Bikramganj, Sabour, Katihar and Araria. When the soil was treated with K_2O (500 mg.%), the % fixation decreased, although the total amount fixed recorded an increase. Higher % fixation at 250 mg. % of K_2O than that at higher concentration appears to correspond to the findings of Joffe and Levine[3] who reported that larger proportions of applied K were fixed at lower concentration. The present data are also in agreement with the findings of Mehta and Shah[8] who found an increase in K fixation with increase in concentration of the applied K till about 750 mg.% of K_2O after which it remained practically constant.

Effect of large excess of calcium:—The increase in the K fixation of various soils after pretreatment with large excess of calcium is reported in Table 3.

Such an increase in potassium fixation was noted by several workers including Wiklander.[15] Kelley[5] and York & Rogers[16] explained the increase in the fixation of potassium at high pH as due to increase in the solubility of SiO_2 and $Al(OH)_3$ resulting in the formation of insoluble potassium-alumino-silicate of permutite like structure.

An increase in the fixation of potassium (more than 100%) in the soils of Chaibasa, Ranchi and Hazaribagh is rather unusual as these soils are more kaolinitic in nature than illitic. This may be due to rise of pH but in view of

TABLE 3

Potassium Fixation in Presence of Large Excess of Calcium

Soils	Percent fixation		% increase
	Before treatment	After treatment	
Chaibasa ...	12·64	41·76	230·2
Putida ...	39·75	67·86	70·70
Ranchi ...	−6·64	47·78	850·1
Giridih ...	29·71	33·80	13·7
Hazaribagh ...	17·66	35·73	102·3
Gaya ...	29·71	43·76	47·2
Nawadah ...	29·71	47·78	64·1
Bikramganj ...	25·67	41·75	62·6
Patna ...	47·78	55·82	16·8
Sabour ...	23·68	45·77	93·7
Katihar ...	26·02	39·75	52·7
Araria ...	18·66	45·77	145·0
Saharsa ...	43·76	53·81	22·9
Raxaul ...	43·76	47·78	8·4

other soils of identical acidity where such phenomenal increase in fixation has not taken place, the pH theory has to be discounted. Further, it can not be said definitely that calcium hydroxide treatment has caused an expansion of the lattice of kaolinite, though the fixed lattice of kaolinite has been known to expand under certain conditions. In remaining soils, where illite is the dominating clay mineral, the mechanism of fixation may be attributed to the expansion of crystal lattice. Results of several workers, viz., Mehta and Shah,[8] Wiklander[15] and McLean[7] also suggest that liming of acid soils increases potassium fixation.

Effect of removal of organic matter:—The effect of removal of organic matter by H_2O_2 and bromine water on K fixation is shown in Table 4.

These results show that the fixation of potassium decreased with the oxidation of organic matter with hydrogen peroxide and the reduction was generally more pronounced in the case of bromine water treatment of soils. It may be that since the bromine water is a stronger oxidising agent than hydrogen peroxide, there may be some break down of lattice in addition to the removal of organic matter. Schuffelen as quoted by Schuffelen and van der Marel[13] indicated smaller decrease with bromine water than hydrogen peroxide because of NH_4 decomposition.

There is hardly any agreement between workers in this field on the effects of removal of organic matter on K fixation. Hauser[2] and Martin *et al.*[6] have reported decrease in fixation of K due to the fixation of ammonium ions which are set free due to oxidation. Pathak *et al.*,[10] Karim & Malek[4] and others, on the other hand, reported an increase in K fixation due to removal of organic matter. According to them, removal of organic colloidal coating on the surfaces of the minerals facilitates in the free passage of ions to crystal lattice.

TABLE 4

Potassium Fixation After Removal of Organic Matter

Soils	Percent fixation			Percent decrease	
	No treatment	H_2O_2 treatment	Br-water treatment	H_2O_2	Br-water
Chaibasa ...	12·64	0·47	0·35	96·28	97·24
Putida ...	39·75	5·08	7·46	89·76	81·23
Ranchi ...	−6·64	−9·90	−2·66	−50·00	64·00
Giridih ...	29·71	12·88	7·22	56·64	75·70
Hazaribagh ...	17·66	2·99	1·39	82·10	92·13
Gaya ...	29·71	23·42	7·45	21·13	74·53
Nawadah ...	29·71	7·34	9·75	75·29	66·18
Bikramganj ...	25·67	4·16	0·35	82·23	98·63
Patna ...	47·78	23·42	3·36	50·98	92·97
Sabour ...	23·68	7·70	3·47	67·48	85·31
Katihar ...	26·02	4·56	9·74	86·31	82·56
Araria ...	18·66	7·77	9·60	58·73	48·55
Saharsa ...	43·76	11·25	3·36	74·28	92·32
Raxaul ...	43·76	3·44	3·00	92·38	91·88

Summary

The effects of various factors, such as wetting and drying, addition of large amounts of K or Ca to soils and removal of organic matter from the soils on K fixation were investigated in representative soil samples of Bihar belonging to both sedentary and alluvial groups. Alternate wetting and drying of soils increased K fixation from 23 to 476%. Increasing the concentration of applied K from 100 to 500 mg. K_2O per 100 g. of soils resulted in the increase of the amounts of K fixed. Percentage of fixation, however, was maximum at 250 mg. K_2O application. Application of large excess of Ca (200 mg.%) also resulted in the increase of K fixation from about 10 to over 200%. Roughly 20 to 100% decrease in K fixation was observed on removal of organic matter from soils, bromine water being more effective than hydrogen peroxide in reducing the K fixation.

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POLAROGRAPHIC STUDY OF THE COMPLEXES FORMED BY CADMIUM WITH OXALATE IONS

By

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Polarography supplies a basis for calculating the stability constants of complexes when the free metal ion and the complex are reduced reversibly, namely, when the rate of the electrode reaction (electron transfer) is considerably greater than that of the diffusion process which as the slowest controls the overall rate. It has been known that cadmium forms complexes with various complexing agents. The polarography of cadmium complexes with various ligands have been studied by a number of workers.[1-8] During polarographic investigation of cadmium in various base electrolytes, it was found that cadmium is reversibly reduced in potassium oxalate solution and the reduction is diffusion-controlled. The shift of half-wave potential towards more negative side with the increasing oxalate concentration showed the complex formation between cadmium and oxalate ion. The present paper deals with the determination of composition and stability constants of the complexes formed by Cd^{2+} with oxalate ions using polarographic method.

EXPERIMENTAL

Reagent grade chemical were used throughout the investigation. The solution of cadmium was prepared by dissolving a weighed amount of cadmium nitrate in distilled water and standardised as usual. Potassium oxalate was used as complexing agent and potassium nitrate to keep constant ionic strength. Triton X_{100} as supplied by Rohm and Hass Co. was employed as maxima suppressor.

Polarograms were recorded manually after de-aeration by a Heyrovsky system LP 55 Polarograph. The half-wave potentials were checked by a W.G. Pye vernier potentiometer. The D.M.E. had the following characteristics: $m = 1{\cdot}76$ mg/sec. and $t = 4{\cdot}5$ sec. (in 0·1M potassium nitrate solution at -1·0 V Vs S.C.E.). The measurements were done at $30 \pm {\cdot}01°C$ which was controlled by a Haake type ultra thermostat. The reversibility of the reduction was tested by the slopes of the plot of $\log i/(i_l - i)$ vs E . Purified nitrogen was used for de-aeration. Solutions containing 0·4mM cadmium and 0·0, 0·05, 0·07, 0·1, 0·15, 0·2, 0·25, 0·3, 0·35, 0·4, 0·45 and 0.5 M potassium oxalate concen-

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tration, were prepared. Requisite amount of potassium nitrate was added to maintain the ionic strength at 1·5. Sodium perchlorate could not be used as it caused precipitation of sodium oxalate when the solutions were mixed. The solutions, after through mixing, were placed in the thermostat for 18 hours to ensure complete reaction and uniform temperature.

Theory

It was shown by DeFord and Hume[10] that the shift in half-wave potential due to complex formation can be expressed as follows:

$$\Delta E_{\frac{1}{2}} = (E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s = \frac{2.303RT}{nF} \log_{10} Y \frac{I_c}{I_s} \sum_{0}^{N} \frac{\beta_j \{x\}^j}{Y_{MX_j}} \qquad \ldots\ldots(1)$$

where $(E_{\frac{1}{2}})_c$ and $(E_{\frac{1}{2}})_s$ are the half-wave potentials of the complex and simple metal ions respectively ; R, T and F have their usual significance ; n denotes the number of electrons ; I_s and I_c are the experimental diffusion contants for the simple ion and for all-complex ions respectively ; βj is the overall formation constant of the jth complex ; X is the activity of the complexing ligand, while Y_M and Y_{MXj} denote the activity coefficients at the electrode surface of the metal and complex species respectively. Equation (1) can be re-arranged to define a function F_o ([X]), such as:

$$F_o([x]) = \text{antilog}_{10}\left(\frac{0.434nF}{RT} \Delta E_{\frac{1}{2}} + \log \frac{I_s}{I_c}\right) = YM \sum_{0}^{N} \frac{\beta_j [x]^j}{Y_{MXj}}$$

$$1 + \beta_1 (x) \frac{Y_M Y_x}{Y_{MX1}} + \beta_2 (x)^2 \frac{Y_M (Y_x)^2}{Y_M X_2} + \beta_3 (x)^3 \frac{Y_M (Y_x)^3}{Y_{MX3}} + \qquad \ldots(2)$$

$$F_1([x]) = \frac{F_o([x]) - \beta_0 / Y_s}{C_x Y_x} \qquad \ldots(3)$$

$$F_2([x]) = \frac{F_1([x]) - \beta_1 / Y_{MX1}}{C_x Y_x} \qquad \ldots(4)$$

$$F_3([x]) = \frac{F_2([x]) - \beta_2 Y_{MX2}}{C_x Y_x} \qquad \ldots(5)$$

where [X] denotes the concentration of the complexing ligand, and Y_x is the corresponding activity coefficient. Values of F_o ([X]) for different concentrations of the complexing ligand can be determined experimentally, and Equation (2) can then be solved graphically for β_1, β_2 & β_3.

Further calculations show that the ratio of the uncomplexed metal ion to the various complex species as a function of ligand concentration, can be obtained from the following equations:

$$\frac{[M]}{C_M} = \frac{1}{F_o([x])} \qquad \ldots(6)$$

$$\frac{[MX_j]}{C_M} = \frac{\beta_j x^{]j}}{F_o[x]} \qquad \ldots(7)$$

where [M] denotes the concentration of uncomplexed metal ions, [MXj] = the concentration of the j^{th} complex species, and C_M = the total metal ion added to the system.

Results and Discussion

In each case a well defined single reduction wave appeared. The plot of i_d vs $\sqrt{h}$ was found to be linear which passes through origin and the temperature coefficient was found to be of the order of 1·1% showing that the reduction is diffusion controlled. The plots of log $i/i_d - i$ vs $E_{d.e.}$ were found to be linear with a slope of the order of 30 ± 2 mV which shows that the reduction is a reversible process. The plot of the $E_{\frac{1}{2}}$ vs $-\log C_x$ (C_x = oxalate concentration, Moles) comes to a curve, which showed the formation of two or more complex ions which are in equilibrium. The classical method due to Lingane[9]

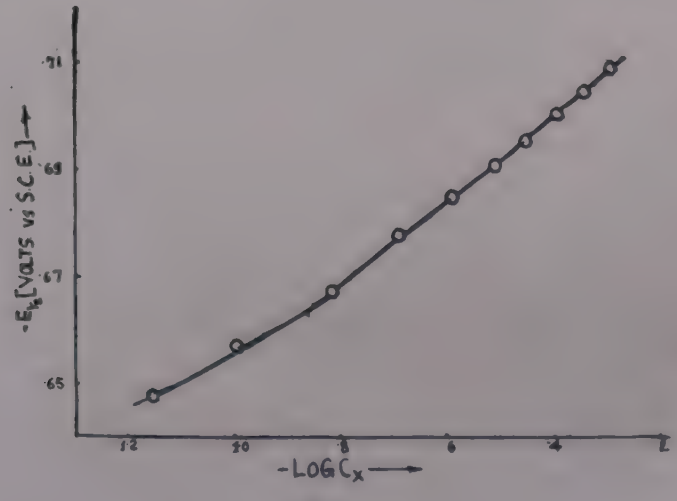

FIG. 1
Plot of $E_{\frac{1}{2}}$ *vs* $\text{Log}c_x$ for
Cadmium—Oxalate System.

could not be applied. For this purpose, DeFord and Hume's method for stepwise complex formation has been applied.[10]

The experimentally determined values of half-wave potentials, together with the Fj ([X]) values obtained from equations (1), (2), (3) and (4) are

TABLE 1

Analysis of F ([X]) function

Sl. No.	Oxalate conc (Moles)	$-E_{\frac{1}{2}}$ (V vs S.C.E.)	i d (Div.)	Slope (mV)	$F_0([X])$	$F_1([X])$	$F_2([X])$	$F_3([X])$
1	0·0	·5862	62·5	32	—	—	—	—
2	0·05	·6383	59	31	57·41	—	—	—
3	0·07	·6474	59	31	115·1	1672	15314	75914
4	0·1	·6565	59	32	231·7	2307	17070	70700
5	0·15	·6688	59·5	32	589·3	3931	22206	81373
6	0·2	·6773	58·5	33	1148	5735	25675	78375
7	0·25	·6847	58·5	33	2021	8080	29920	79680
8	0·3	·6906	58·5	33	3175	10766	33886	79620
9	0·35	·6958	57·5	33·5	4823	13771	43605	79945
10	0·4	·7008	57·5	33·5	7218	18042	37631	84012
11	0·45	·7046	56·5	33·5	9658	21460	46333	80740
12	0·5	·7088	56·5	34	12710	25418	49639	79278

given in Table I, assuming that the ionic atmosphere and, therefore, the several activity coefficients probably changed very little since the ionic strength is constant. The overall formation constants were obtained by a graphical extrapolation (Fig. 2 & 3) of the F ([X]) functions to the zero ligand concentration. The values of the three overall formation constants for the complex ions $Cd(C_2O_4)$, $Cd(C_2O_4)_2^{2-}$ and $Cd(C_2O_4)_3^{4-}$ were found to be $\beta_1=600$, $\beta_2=10000$ and $\beta_3=79000$ ($\mu=1{\cdot}5$, at 30°C) respectively. The above system has been studied by Vosburgh[11] and Clayton[12] using solubility measurements and by Korshunov[13] by ion exchange equilibria. All these workers have reported the

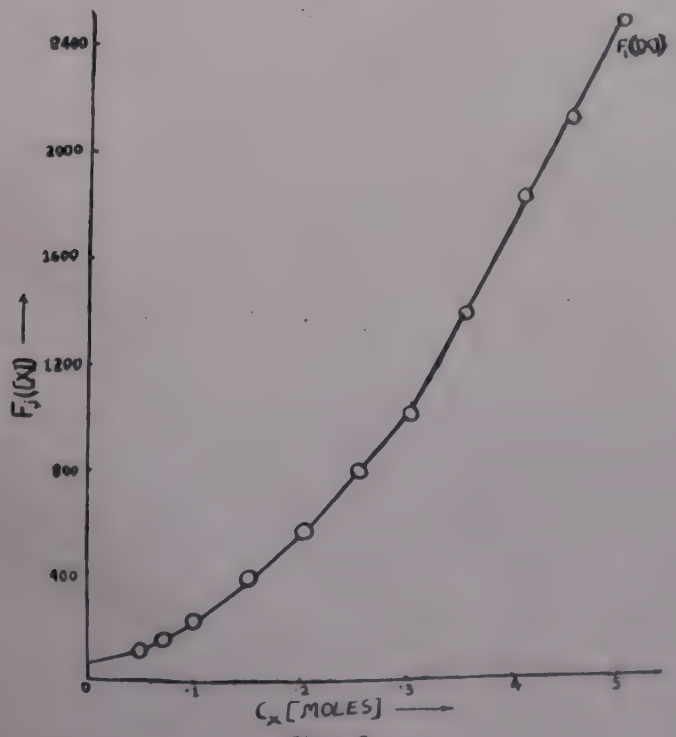

FIG. 2

Plot of $F_1(x)$ *vs* C_x for Cadmium Oxalate System.

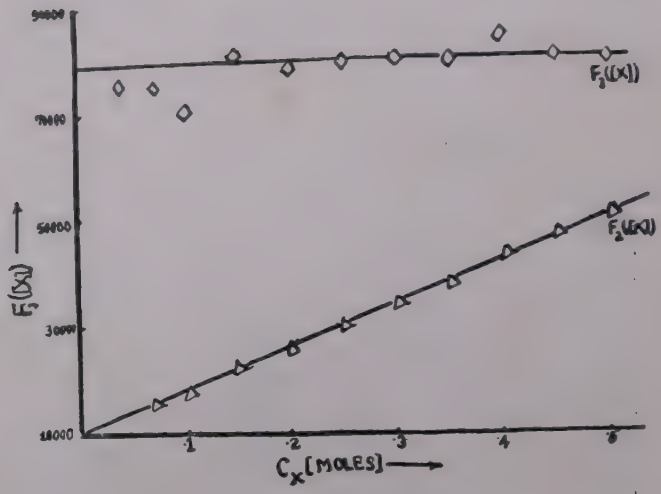

FIG. 3
Plot of $F_3(x)$ *vs* C_x for Cadmium Oxalate System.

formation of one complex ion, $Cd(C_2O_4)_2^{2-}$. Contrary to the above results, we have obtained three complex ions. The controversy can be explained that the earlier workers have not kept the constant ionic strength and have studied the complex formation at low concentration of oxalate ion.

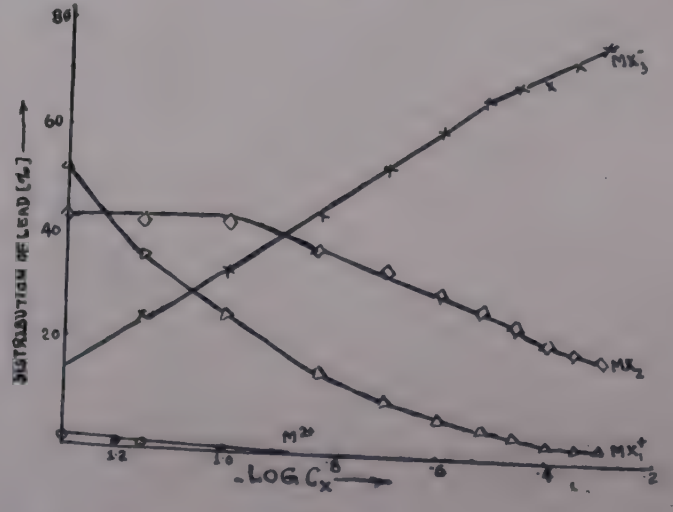

FIG. 4
Plot of Percentage Distribution of Cadmium in various Forms *vs* Log C_x for Cadmium Oxalate System.

The percentage distribution of cadmium present (in the cationic or anionic form) as a function of logarithm of oxalate concentration has been presented in Fig. 4.

SUMMARY

The reduction of cadmium in oxalate media is found to be reversible and diffusion-controlled. The $E_{\frac{1}{2}}$ shifts towards more negative side with the increase of oxalate concentration showing the formation of complexes between

cadmium and oxalate ions. The stability constants of the complexes formed are calculated by DeFord and Hume's method. Three complexes $Cd(C_2O_4)$, $Cd(C_2O_4)_2^{2-}$ and $Cd(C_2O_4)_3^{4-}$ were found having overall constants. $\beta_1 = 600$, $\beta_2 = 10000$ and $\beta_3 = 79000$ ($\mu = 1{\cdot}5$, at 30°C). The percentage distribution of cadmium in various forms as a function of logarithm of oxalate concentration has been presented.

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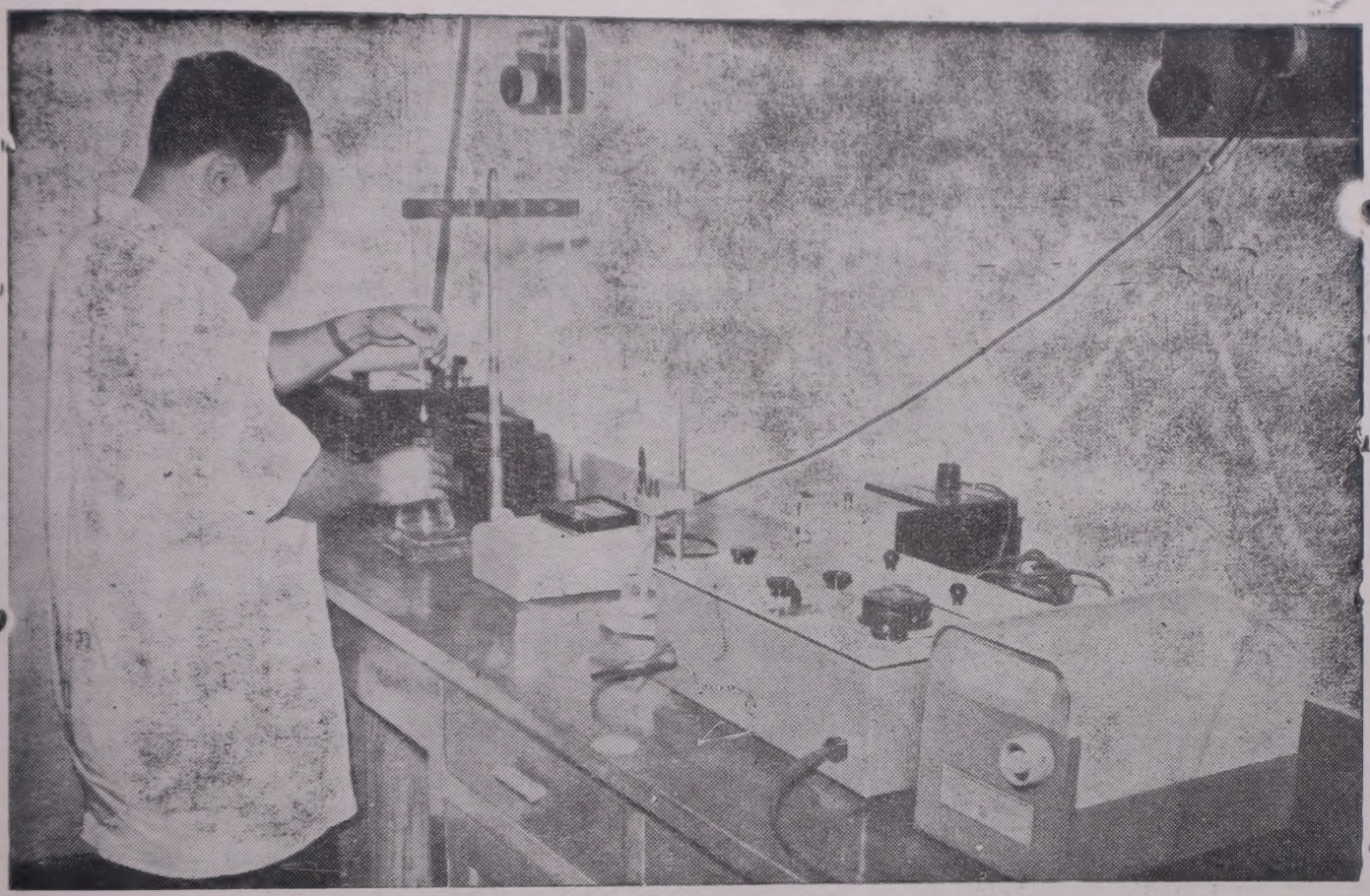

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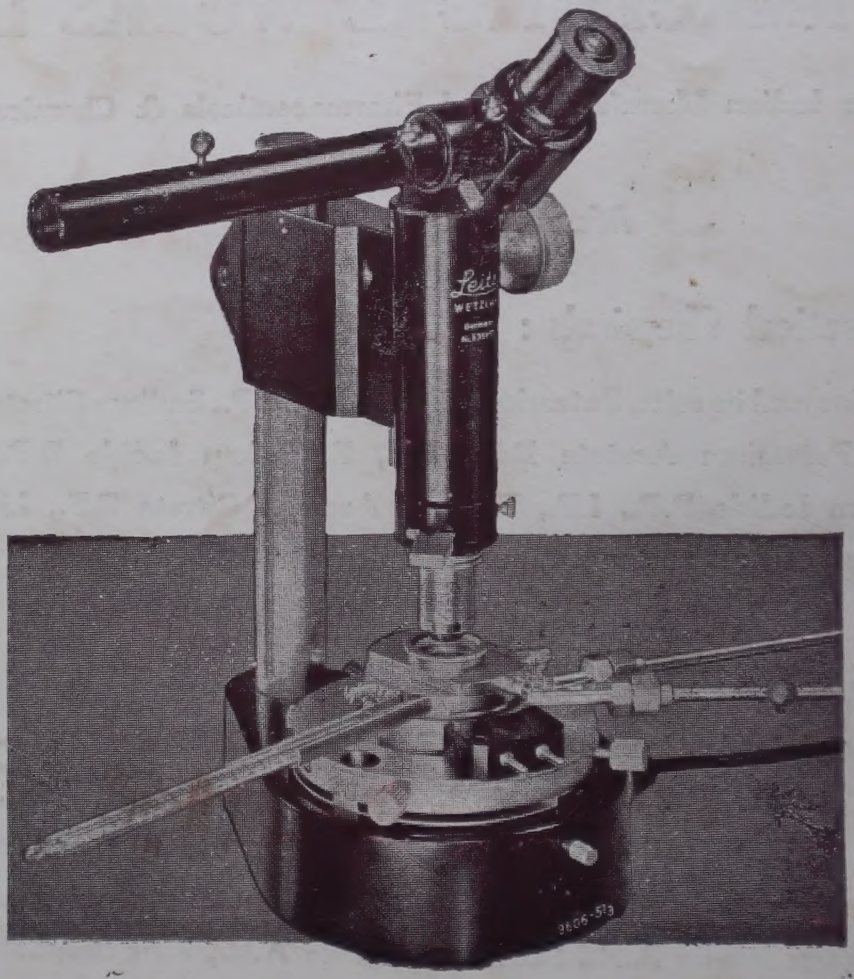

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